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Third Edition

Chemistry of Pyrotechnics

Basic Principles and Theory

John A. Conkling • Christopher J. Mocella

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Preface to the Third Edition: 2019

This book is a continuation of the lifelong work and dedication of Dr. John Conkling, whom I have had the distinct honor to work for. While Dr. Conkling has “retired” from primary work on *The Chemistry of Pyrotechnics*, the reader should make no mistake that this is still entirely his work, and his are the shoulders that I stand on.

I met Dr. Conkling in 1999 while working at Washington College in Chestertown, MD (both our alma mater) between school years as I worked for the summer conferences held there, one of which was his legendary Summer Pyrotechnics Seminar. At that time a good friend of mine was also his research fellow and, seeing the opportunity, I inquired and later became Dr. Conkling’s summer research fellow. I completed my undergraduate research under his tutelage, concurrently becoming a member of the pyrotechnics seminar instructional staff, and continued through its final 27th year in 2010. Dr. Conkling continues to advise on this project and many other pyrotechnics and fireworks ventures out there, and I cannot express my gratitude enough for his mentorship, both academic and professional, and continued friendship to this day.

In continuing Dr. Conkling’s work with this text, I have strived to take the core discussion of chemistry and pyrotechnics and update the main themes with recent advancements since the previous version was published, most notably in the world of “green pyrotechnics” and finding new formulations with decreased toxic effects to humans and the environment around us. The amount of research going into new pyrotechnic study is extensive, and I was able to include only a small segment of what is out there. I hope the reader will be inspired to use the many references and ideas to continue their own research and advance the state-of-the-art of pyrotechnics well into the 21st century.

Christopher J. Mocella
Annapolis, MD

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Preface to the Second Edition: 2010

In the twenty-five years that have passed since the first edition of this book was published, the world of pyrotechnics and high energy materials has continued to undergo significant changes. The changes have been driven primarily by concerns for safety - of personnel working with energetic materials, of the communities located near facilities producing energetic materials, as well as concerns for the environment. One result of the pressure for change has been the promulgation of new government regulations placing restrictions on the materials that may be used in energetic mixtures, mandating numerous training programs, and initiating other actions - such as OSHA's Process Safety Management Standard - intended to eliminate accidents and incidents. And almost all of the personnel who entered the field of energetic materials in the 1950's and 1960's have now retired and taken with them their years of hands-on, practical knowledge in the preparation of energetic mixtures.

The International Pyrotechnics Seminars have grown in frequency and significance since the first edition of this book was published in 1985. There is now at least one seminar a year, either in Colorado or a non-United States location, and the proceedings from these seminars continue to be a great source of information regarding ongoing pyrotechnic research. In addition, the International Symposium on Fireworks (ISF) continues to be held every other year in Canada or elsewhere and these sessions always produce an interesting blend of technical papers.

The Pyrotechnics Guild International (PGI) has matured into a respected group of pyrotechnics enthusiasts and researchers who are making significant contributions in the area of fireworks technology.

A new journal, appropriately named *The Journal of Pyrotechnics*, has provided a vehicle for the prompt publication of research and review papers in the broad field of pyrotechnics.

On the negative side, we in the United States continue to lack any organized, broad-range academic programs covering the science of energetic materials. The New Mexico Institute of Technology is offering a program in explosive technology, and this is a great first step. More and more, the field of pyrotechnics is interacting with and adapting to changing technology in areas such as obscuration science and low-signature flame emission. Greater academic interest in the science of pyrotechnics would be a valuable asset for this country.

I'd like to thank my numerous colleagues and co-workers over the past twenty-five years for their interesting discussions, helpful comments, and constructive criticism. First on the list is Joseph Domanico, my friend and colleague with the Summer Pyrotechnic Seminar program at Washington College since 1984 – Joe is truly a unique individual with a broad knowledge of the field of energetic materials.

I also want to thank Christopher J. Mocella, Washington College '01 for his assistance with, and contributions to, the second addition of this book. Chris also participates as an instructor in the Summer Pyrotechnic Seminars at Washington College, and has become a valuable member of the team.

The thank-you list includes Tom Shook and Loy Aikman at Pine Bluff Arsenal, who got me involved in the military side of pyrotechnics two decades ago. Another special acknowledgement goes to David Pier of MP Associates, with whom I have enjoyed debating a wide variety of topics covering many aspects of energetic material for many years. Other friends and colleagues who have contributed to my education include the late Fred McIntyre, and another former Washington College chemistry student Jeff Johnson, with Orion Safety Products. I'd also like to thank the American Pyrotechnics Association for allowing me time to pursue my scientific interests for many years, and to TNT Fireworks and Orion Safety Products for allowing me to assist them with interesting projects since my retirement for the APA. More thanks go to the participants in my Summer Pyrotechnic Seminar programs for the past 27 years, and to my friends at the Bureau of Alcohol, Tobacco and Firearms, and Judy LeDoux and Debra Satkowiak in particular, for allowing me to assist them with training for their personnel.

Finally, I must acknowledge the importance of my wife Sandra to this project, without whose persistent encouragement this second edition would have been delayed even more. Aiding her in this motivational effort have been my two children, Melinda Conkling Hart and John A. Conkling, Jr., who in addition have presented us with four wonderful Texas grandchildren – John Maxey Hart, Edward Austin Hart, Jr., Julia Valliant Conkling, and the newest arrival John A. Conkling III. Maybe one of them will go on to a career in this fascinating field.

This book continues to stress basic chemical principles, rather than serve as a "how-to" guide for pyrotechnics. There are detailed published works covering many areas of energetic materials in detail. This book is intended as a bridge to allow people to transition with confidence from a knowledge of chemistry to an ability to apply chemical principles and logic to energetic materials. Discussion of the historical past of the field of pyrotechnics is, regrettably, kept to a minimum. The history of this field - particularly the work in the 20th century - is another book waiting for someone to pursue, but there should be no doubt in anyone's mind that pyrotechnics - like any other field of science - can only grow and expand as a science by building on past accomplishments in the field. Everyone's goal must continue to be to make the field of energetic materials as productive and useful, and as safe, as we possibly can.

John A. Conkling
Chestertown, MD

Preface to the First Edition: 1985

Everyone has observed chemical reactions involving pyrotechnic mixtures. Beautiful 4th of July fireworks, highway distress signals, solid fuel boosters for the Space Shuttle, and the black powder used by muzzle-loading rifle enthusiasts all have a common technical background.

The chemical principles underlying these high-energy materials have been somewhat neglected in the twentieth century by academic and industrial researchers. Most of the recent work has been goal-oriented rather than fundamental in nature (e.g., produce a deeper green flame). Many of the significant results are found in military reports, and chemical fundamentals must be gleaned from many pages of test results.

Much of today's knowledge is carried in the heads of experienced personnel. Many of these workers acquired their initial training during World War II, and they are presently fast approaching (if not already past) retirement age. This is most unfortunate for future researchers. Newcomers have a difficult time acquiring the skills and the knowledge needed to begin productive experiments. A background in chemistry is helpful, but much of today's modern chemistry curriculum will never be used by someone working in pyrotechnics and explosives. Further, the critical education in how to safely mix, handle, and store high-energy materials is not covered at all in today's schools and must be acquired in "on-the-job" training.

This book is an attempt to provide an introduction to the basic principles of high-energy chemistry to newcomers and to serve as a review for experienced personnel. It can by no means substitute for the essential "hands on" experience and training necessary to safely work in the field, but I hope that it will be a helpful companion. An attempt has been made to keep chemical theory simple and directly applicable to pyrotechnics and explosives. The level approaches that of an introductory college course, and study of this text may prepare persons to attend professional meetings and seminars dealing with high-energy materials and enable them to intelligently follow the material being presented. In particular, the International Pyrotechnic Seminars, hosted biannually in the United States by the Illinois Institute of Technology Research Institute in conjunction with the International Pyrotechnics Society, have played a major role in bringing researchers together to discuss current work. The Proceedings of the nine seminars held to date contain a wealth of information that can be read and contemplated by persons with adequate introduction to the field of high-energy chemistry.

I would like to express my appreciation to Mr. Richard Seltzer of the American Chemical Society and to Dr. Maurits Dekker of Marcel Dekker, Inc. for their encouragement and their willingness to recognize pyrotechnics as a legitimate branch of modern chemistry. I am grateful to Washington College for a sabbatical leave in 1983 that enabled me to finalize the manuscript. I would also like to express my thanks to many colleagues in the field of pyrotechnics who have provided me with data as well as encouragement and to my 1983 and 1984 Summer Chemistry Seminar groups at Washington College for their review of draft versions of this book. I also appreciate the support and encouragement given to me by my wife and children as I concentrated on this effort.

Finally, I must acknowledge the many years of friendship and collaboration that I enjoyed with Mr. Joseph H. McLain, former Chemistry Department Chairman and subsequently President of Washington College. It was his enthusiasm and encouragement that dragged me away from the norbornyl cation and physical organic chemistry into the fascinating realm of pyrotechnics and explosives. The field of high-energy chemistry lost an important leader when Dr. McLain passed away in 1981.

John A. Conkling
Chestertown, MD

Authors

Dr. John A. Conkling received his BSc degree from Washington College in Chestertown, Maryland, in 1965 and his PhD in chemistry from Johns Hopkins University in 1969. Dr. Conkling returned to Washington College as a chemistry professor and colleague of Dr. Joseph McLain, who at the time was studying energetic materials and pyrotechnics, which Dr. Conkling began to study for his career. As former executive director and technical director of the American Pyrotechnics Association, Dr. Conkling is widely regarded as one of the world's foremost experts in pyrotechnics. Dr. Conkling conducted "The Summer Pyrotechnic Seminar" at Washington College for 29 years, and he is the original author of *Chemistry of Pyrotechnics: Basic Principles and Theory* in 1985 and second edition in 2010. Dr. Conkling retired from Washington College in 2012 and was awarded the Alumni Service Award in 2013. Dr. Conkling currently splits his time between Chestertown and Texas to be with his family.

Christopher J. Mocella received his BSc degree in chemistry from Washington College in Chestertown, Maryland, in 2001, having studied as a research associate under Dr. John Conkling. Chris continued to work with Dr. Conkling at his Summer Pyrotechnics Seminar series and assisted with the second edition of the Chemistry of Pyrotechnics text. Following graduate studies in chemistry at the University of Virginia, Chris took a position as a chemist with the U.S. federal government where he continues his career today. Chris lives with his wife and son near Annapolis, Maryland.

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1 Introduction

Red, white, and blue bursts highlight at 4th of July fireworks spectacular.

Welcome to the world of energetic materials. Few people plan to spend their professional careers in this field of science and technology, but there is an old saying that "once you smell the smoke," you are hooked.

A PRIMER ON ENERGETIC MATERIALS

This book is an introduction to the basic principles and theory of pyrotechnics, with a focus on the chemistry and chemical interactions of the materials involved.

The term "pyrotechnics" comes from the Greek noun *pyr* for "a fire," and *techne* for "art," "craft skill," or "technique," which today might also be thought of as "science." Therefore, we might think of pyrotechnics as the "art of fire" or the "science of fire" and, as the reader will see, both scientific principles as well as some artistic creativity go into all pyrotechnic work.

Much of the "pyrotechnics" material in this text is also applicable to the closely related areas of propellants and explosives, all of which fall under the broad umbrella of "energetic materials" as shown in Figure 1.1. *Propellants* are designed to "deflagrate," or burn considerably rapidly—but not quite explode—under the confinement of a rocket engine or a gun barrel (noting that many propellants burn rather mildly

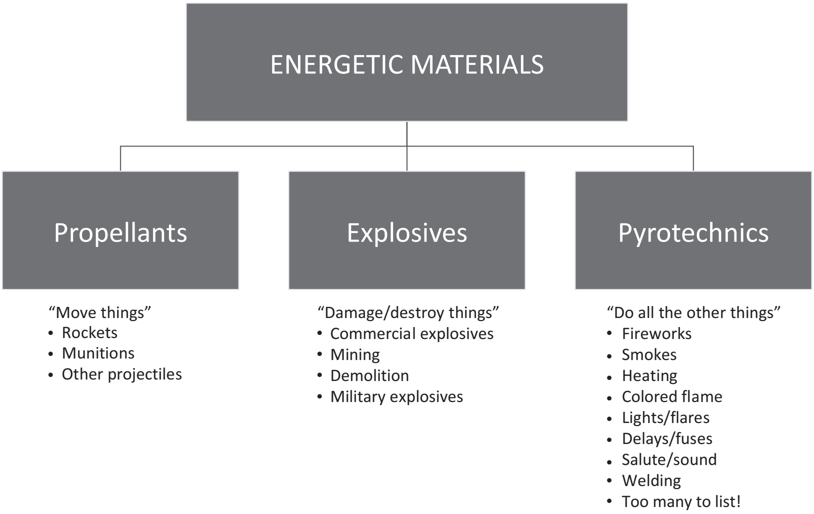

FIGURE 1.1 This chart shows a breakout of the disciplines of "energetic materials," classified as propellants (which move objects), explosives (which damage or destroy objects), and pyrotechnics (which is a catch-all for the many other functions that energetic materials can perform). While one could consider propellants and explosives types of pyrotechnics, the breadth and depth of the applications and study going into each affords them categories all their own.

in the open when unconfined). Propellants are formulated to maximize the volume of hot gas produced as the propellant material rapidly burns, pushing the hot gas out and, hopefully, the projectile in the intended direction. *Explosives* rapidly release large amounts of energy, and explosives engineers take advantage of this rapid release of energy, and the associated shock and pressure, to do work, often through a full "detonation" event (the difference between deflagrations and detonations will be discussed in a later chapter).

Pyrotechnic mixtures, our primary interest here, usually (but not always) react more slowly than explosive or propellant compounds, and the heat generated by the burning chemical mixture is used to produce combinations of light, color, smoke, gas, heat, and noise for a wide range of applications. Pyrotechnics, additionally, will combust as a smolder, as a fast burn, or as a full "deflagration" as opposed to a nearly instantaneous "detonation" of high explosives. Notably, a well-established research journal by the name *Propellants, Explosives, Pyrotechnics* has been publishing peer-reviewed research since 1976. The terms "high-energy chemistry" and "energetic materials" are also used to refer to these three closely related fields as a group.

The chemical reactions involved in pyrotechnics are of the classic electron-transfer or oxidation-reduction type (also colloquially referred to as "redox" reactions). Here, chemical species interact, exchange electrons, form new products, and release any excess energy. The mixtures to be studied are almost always solids at room temperature and are designed to function in the absence of external oxygen. Table 1.1 illustrates the reaction rates to be dealt with in that range along a continuum from very

TABLE 1.1
Classes of "High-Energy" Reactions

Class	Approximate Reaction Velocity	Example
Burning	Millimeters per second (mm/s)	Delay mixtures, colored smoke compositions
Deflagration	Meters per second (m/s)	Rocket propellants, confined black powder
Low-order detonation	>1 Kilometer per second (km/s)	Dynamite, TNT
High-order detonation	>5 km/s	Military explosives

slow burning to "instantaneous" detonations with rates greater than a kilometer/second. We should note that "detonation" refers to a specific, shock-propagated process for the reaction of an energetic material—the term "detonation" is *not* synonymous with "ignition" or "explosion." A detonation is an explosion, but so are high-rate deflagrations (especially when the material is confined).[1]

BLACK POWDER: THE ORIGINAL PYROTECHNIC

It is important to recognize early on that the same material may vary dramatically in its reactivity depending on its method of preparation and the conditions under which it is used. Black powder is an excellent example of this variability, and it is quite fitting that it serves as the first example of a "high-energy material" due to its historical significance (Kelly 2004; Buchanan 1996). Black powder is an intimate mixture of potassium nitrate (~75% by weight), charcoal (~15%), and sulfur (~10%), and its unique properties and characteristics continue to intrigue researchers even today (Brown and Rugunanan 1989; Hussain and Rees 1992; Maltitz 2001). A reactive black powder is no simple material to prepare and is a classic example of the "art" of manufacturing pyrotechnics. If one gently mixes the proper ratio of three components briefly, a powder is produced that is difficult to light and burns quite slowly. The same ingredients in the same proportions—when thoroughly mixed, moistened, and ground with a heavy stone wheel to achieve a high degree of homogeneity—become a mixture that readily ignites and burns rapidly. Particle size, purity of the starting materials, mixing time, and a variety of other factors—including the type of wood used to prepare charcoal—are all critical in producing high-performance black powder. Also, deviations from the 75/15/10 ratio of ingredients will lead to substantial changes in performance. Much of the early history of modern Europe is related to the availability of high-quality black powder for use in rifles and cannons. A good black powder manufacturer was essential to military success although he usually received far less recognition and decoration than the generals who used his product in their battles.

The burning behavior of black powder illustrates how a pyrotechnic mixture can vary in performance depending on the conditions of its use. A small pile of loose black powder can be readily ignited by the flame of a match, producing an orange flash and a puff of smoke—but almost no noise. The same powder, tightly sealed in a strong paper tube but still in loose condition, will explode upon ignition by means of a fuse, rupturing the container with an audible noise. Black powder spread in a thin trail will quickly burn along the trail, a property used in making early fuses. Finally, if the powder is compressed in a tube, one end is left open, and that end is then constricted to partially confine the hot gases produced when the powder is ignited, a rocket-type device is produced. This varied behavior depending on confinement is quite typical of pyrotechnic mixtures and illustrates why one must be quite specific in giving instructions for preparing and using the materials discussed in this book.

---

[1] All detonations are explosions, but not all explosions are detonations!

Black powder is also a good example to use to illustrate the dramatic effect that moisture can have on pyrotechnic compositions. Damp powder is difficult to light and burns quite slowly—if at all—if ignition is successful. “Keep your powder dry” is still among the best pieces of advice for anyone making or using pyrotechnic materials, and hygroscopic chemicals—those that tend to rapidly pick up moisture in a humid environment—tend to be avoided by pyrotechnic formulators or kept in tight containers in environmentally controlled locations.

Why should someone working in pyrotechnics and related areas bother to study the basic chemistry involved? Throughout the 400-year “modern” history of the United States, many black powder factories have been constructed and put into operation. Although “smokeless powder” (a general term for propellants with more gaseous and less particulate combustion products than black powder, most commonly nitrocellulose-based) and other new materials have replaced black powder as a propellant and delay mixture in many applications, there is still a sizeable demand for black powder in both the military and civilian pyrotechnic industries due to its inexpensive ingredients and consistent properties when consistently prepared and stored. How many black powder factories are still operating in the United States today? Exactly one—GOEX Powder Inc., in Louisiana (GOEX, Inc. 2014). The remainder have been destroyed by explosions or closed because of the probability of one occurring: costs associated with critical worker safety are unable to compete economically with factories in other countries that are not subject to strict safety requirements, a potentially dangerous trade. In spite of a demand for the product, manufacturers are reluctant to engage in the production of the material because of the history of problems with accidental ignition during the manufacturing process. Why is black powder so sensitive to ignition? What can the chemist do to minimize the hazard? Can one alter the performance of black powder by varying the ingredients and their percentages, using theory as the approach rather than trial-and-error?

Black powder is not unique in its properties, however. High-energy materials like propellants and pyrotechnics are all designed to release energy in brief periods of time when an ignition stimulus is applied. New formulations continue to be developed, and new materials continue to be investigated for possible use in novel compositions. A pyrotechnic formulation consisting largely of magnesium powder and polytetrafluoroethylene (PTFE, also the chemical in the DuPont company’s Teflon® product) is used to produce decoy flares for the protection of military aircraft from heat-seeking missiles. This material has acquired a “black powder”-like reputation in recent years. Virtually every manufacturer of this material has suffered an incident producing magnesium-Teflon® composition, and the need to understand the basic science of the material has received much attention (Kubota and Serizawa 1987; Kuwahara, Matsuo and Shinozaki 1997). It is this type of problem and its analysis that we hope can be addressed a bit more thoroughly and scientifically with an understanding of the fundamental concepts presented in this book. If one accident can be prevented as a consequence of someone's better insight into the chemical nature of high-energy materials, achieved through study of this book, then the effort that went into its preparation was worthwhile.

A BRIEF HISTORY AND CULTURAL SIGNIFICANCE

The use of chemicals and chemical mixtures to produce heat, light, smoke, noise, and motion has existed for several thousand years, originating most likely in China or India. India has been cited as a particularly good possibility due to the natural deposits of saltpeter (potassium nitrate, KNO_3) found there (U.S. Army Material Command 1967).

Much of the early use of chemical energy involved military applications. "Greek fire," first reported in the 7th century AD, was probably a blend of sulfur, organic fuels, and saltpeter that generated flames and dense fumes when ignited. It was used in a variety of incendiary ways in both sea and land battles and added a new dimension to military science (U.S. Army Material Command 1967).

At some early time, most likely prior to 1000 AD, an observant scientist recognized the unique properties of a blend of potassium nitrate ("saltpeter"), sulfur ("brimstone"), and charcoal. Black powder was developed as the first "modern" high-energy composition. One interesting conjecture is that Chinese experimenters were searching for an elixir for immortality by mixing the "yin" of potassium nitrate and the "yang" of sulfur to create a "fire drug" (McLain 2017).

The Chinese were involved in pyrotechnics at an early date and had developed rockets by the 10th century (U.S. Army Material Command 1967) and were using black powder filled bamboo sticks thrown into fires to ward off evil spirits (McLain 2017). Fireworks followed, including firecrackers, and Chinese firecrackers became a popular item in the United States when trade was begun between the United States and China in the 1800s. Family correspondence passed down to Dr. John Conkling, the primary author of this book, shows that his great-great-grandfather, a merchant ship captain also named John Alexander Conkling, included "firecrackers" on his personal shopping list for a voyage to Canton, China (now Guangdong, China) in the 1830s. Dr. Conkling was not aware of this until after he had himself become involved in the field of pyrotechnics but was pleased to learn that the Conkling family was among the first importers of Chinese fireworks into the United States.

Chinese fireworks remain popular in the United States today, along with an assortment of other types of pyrotechnic articles that produce a wide assortment of visible and audible effects. The Japanese also produce beautiful fireworks, but, curiously, they do not appear to have developed the necessary technology until fireworks were brought to Japan around 1600 AD by an English visitor (Shimizu 1981). Many of the advances in fireworks technology over the past several centuries have come from these two Asian nations, and China today is the world's primary supplier of both consumer and display fireworks.

The use of pyrotechnic and propellant mixtures for military purposes in rifles, rockets, flares, and cannons developed simultaneously with the civilian applications such as fireworks. Progress in both areas followed advances in modern chemistry, as new chemical compounds were isolated and synthesized and became available commercially to the pyrotechnician. Berthollet's discovery of potassium chlorate in the 1780s resulted in the ability to produce brilliant flame colors using pyrotechnic compositions, and color was added to the effects of sparks, noise, and motion previously available using potassium nitrate-based compositions.

The harnessing of electricity led to the manufacturing of magnesium and aluminum metals by electrolysis in the latter part of the 19th century, and bright white sparks and whiter light could then be produced. Strontium, barium, and copper compounds capable of producing vivid red, green, and blue flames also became commercially available during the 19th century, and modern pyrotechnic technology really took off.

Simultaneously, the discovery of nitroglycerine in 1846 by Sobrero in Italy, and Nobel's subsequent work with dynamite, led to the development of a new generation of true high explosives that were far superior to black powder for many blasting and explosives applications. These materials released their chemical energy through the *detonation* process, at rates much faster—and with greater accompanying blast pressure and shock—than the deflagration process by which propellants and pyrotechnics react upon ignition. The development of modern smokeless powder in the latter part of the 19th century—based on nitrocellulose and nitroglycerine—led to the demise of black powder as the main propellant for guns of all types and sizes.

Although black powder has been replaced in most of its former uses by newer and more energetic materials, it is important to recognize the important role black powder has played in modern civilization. Tenney Davis, addressing this issue in his classic book on the chemistry of explosives, wrote, "The discovery that a mixture of potassium nitrate, charcoal, and sulfur is capable of doing useful work is one of the most important chemical discoveries or inventions of all times... the discovery of the controllable force of gunpowder, which made huge engineering achievements possible, gave access to coal and to minerals within the earth, and brought on directly the age of iron and steel and with it the era of machines and of rapid transportation and communication" (Davis 1941). Black powder remains a viable energetic material today—it ignites readily and reliably and is quite stable in storage if kept dry, and it is commercially available in a range of grain sizes ranging from fine powder to granules the size of kernels of corn. Black powder is also fascinating because it is one of the very few materials produced by the chemical industry that is still made today using essentially the same materials and manufacturing process as it was produced 500 years ago.

Explosives are widely used today throughout the world for mining, excavation, demolition, and military purposes. Pyrotechnics are also widely used by the military for signaling, obscuration, and training simulators. Military technology is constantly striving to keep pace with advances in other areas of technology, such as thermal detection and "night vision" equipment. Civilian applications of pyrotechnics are many and varied, ranging from the common match to highway warning flares ("fusees") to ever-popular fireworks and the spectacular "special effects" used to enhance movies, rock concerts, professional wrestling matches, sporting events, and theme park shows.

The fireworks industry remains perhaps the most visible example of pyrotechnics to the general public and also remains a major user of traditional black powder. This industry provides the pyrotechnician with the opportunity to fully display his skill at producing colors and other brilliant visual effects. The use of fireworks in the United States has not diminished. There has been a steady growth in consumption of fireworks from an estimated 30 million pounds in 1976 to over 285 million pounds in 2015, according to data compiled by the American Pyrotechnics Association (APA 2017).

Fireworks form a unique part of cultural heritage of many countries (Plimpton 1984). In the United States, fireworks have traditionally been associated with Independence Day—The Fourth of July. In England, large quantities are set off in commemoration of Guy Fawkes Day (November 5th), while the French use fireworks around Bastille Day (July 14th). Many countries use fireworks to celebrate the New Year on January 1st. Notably, in Germany, the use of fireworks by the public is limited to *one hour per year*: from midnight to 01:00 a.m. on January 1st—but it is reported to be quite a celebration. Much of the Chinese culture is associated with the use of firecrackers to celebrate New Year's and other important occasions, and this custom has been carried over to the Chinese communities throughout the world. The brilliant colors and booming noises of fireworks appear to have a universal appeal to our basic senses, eliciting "ooh's" and "aah's" from spectators regardless of where the fireworks are displayed—worldwide.

To gain an understanding of how these beautiful effects are produced, we will begin with a review of some basic chemical principles and then proceed to discuss various pyrotechnic systems.

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2 Basic Chemical Principles

BLACK POWDER GRANULES: Black powder granules—the first commercial energetic material that has remained an article of commerce for over 1,000 years. This unique blend of potassium nitrate (saltpeter), charcoal, and sulfur (brimstone) has served as an explosive, a propellant, and a component in pyrotechnic devices such as safety fuses and squibs.

> Most chemistry courses do not discuss energetic materials—explosives, propellants, and pyrotechnics—directly or by name. However, these materials all involve "chemistry in action" and produce their energetic output through chemical reactions. Many of the principles and logical thought processes that are taught in "Chem 101" directly apply to what will be covered in this book. Pyrotechnics are not magic, and the pyrotechnic chemist is no longer viewed as a wizard. When you are working in this field, and things seem to be making no sense, it's time to go back to the basics of science.

ATOMS AND MOLECULES

To understand the chemical nature of pyrotechnics and other energetic mixtures, one must begin at the atomic level. Two hundred years of elegant experiments and complex calculations have led to our present picture of the atom as the fundamental building block of matter. An atom consists of a small, dense nucleus containing

TABLE 2.1
Properties of the Subatomic Particles

Particle	Location	Charge	Mass, a.m.u.[a]	Mass, grams
Proton	In nucleus	+1	1.007	1.673×10^{-24}
Neutron	In nucleus	0	1.009	1.675×10^{-24}
Electron	Outside nucleus	−1	0.00549	9.11×10^{-28}

[a] a.m.u. = atomic mass unit, where 1 a.m.u. = 1.66×10^{-24}g.

positively-charged *protons* and neutral *neutrons*, surrounded by a large cloud of light, negatively-charged *electrons*. Table 2.1 summarizes the properties of these subatomic particles.

A particular *element* is defined by its *atomic number*—the number of protons in the nucleus (which will equal the number of electrons surrounding the nucleus in a neutral atom). For example, iron is the element of atomic number 26, meaning that every iron atom will have 26 protons in its nucleus. Chemists use a one or two-letter symbol for each element to simplify communication; iron, for example, is given the symbol Fe, from the old Latin word for iron, *ferrum*. The sum of the protons plus neutrons found in the nucleus is called the mass number. For some elements, only one mass number is found in nature. Fluorine (atomic number 9, mass number 19, symbol "F") is an example of such an element. Other elements are found in nature in more than one mass number. Iron is found as mass number 56 (91.52% abundance of all iron found in nature), 54 (5.90% abundance), 57 (2.245% abundance), and 58 (0.33% abundance). These different mass numbers of the same element are called *isotopes*[1] and vary in the number of neutrons found in the nucleus and therefore vary in their mass as well. *Atomic weight* refers to the average mass found in nature of all the atoms of a particular element; the atomic weight of iron is 55.847. For calculation purposes, these atomic weights are used for the mass of a particular element. Table 2.2 contains symbols, atomic numbers, and atomic weights for the elements. In practical terms, only elements 1–83 (hydrogen through bismuth) have use for "everyday" chemistry, since elements after bismuth are generally radioactive, expensive, inconvenient/unsafe to work with, or all three. Furthermore, the "transuranics" (beyond uranium) of 93 (neptunium) through 118 (oganesson) are either quite radioactive and unsafe to handle in normal circumstances or only exist for fractions of a second—after being synthesized in incredibly complex equipment—before decaying into lighter elements.

Chemical reactivity, and therefore pyrotechnic and explosive behavior, is determined primarily by the tendency for each element to gain or lose electrons during a chemical reaction. Calculations of theoretical chemists, with strong support from experimental studies, suggest that electrons in atoms are found in "orbitals" or

---

[1] The term "isotope" has been commonly and incorrectly used to mean "radioactive material" since certain isotopes of elements can be significantly radioactive, emitting gamma rays, neutrons, alpha particles, or beta particles. However, isotopes of elements are not necessarily radioactive, only those referred to as "radioisotopes" or "radionuclides."

TABLE 2.2
Symbols, Atomic Weights, and Atomic Numbers of the Elements

Element	Symbol	Atomic Number	Atomic Weight, a.m.u.[a]
Actinium	Ac	89	[227][b]
Aluminium	Al	13	26.9815386
Americium	Am	95	[243]
Antimony	Sb	51	121.760
Argon	Ar	18	39.948
Arsenic	As	33	74.92160
Astatine	At	85	[210]
Barium	Ba	56	137.327
Berkelium	Bk	97	[247]
Beryllium	Be	4	9.012182
Bismuth	Bi	83	208.98040
Bohrium	Bh	107	[272]
Boron	B	5	10.811
Bromine	Br	35	79.904
Cadmium	Cd	48	112.411
Cesium	Cs	55	132.9054519
Calcium	Ca	20	40.078
Californium	Cf	98	[251]
Carbon	C	6	12.0107
Cerium	Ce	58	140.116
Chlorine	Cl	17	35.453
Chromium	Cr	24	51.9961
Cobalt	Co	27	58.933195
Copper	Cu	29	63.546
Curium	Cm	96	[247]
Darmstadtium	Ds	110	[281]
Dubnium	Db	105	[268]
Dysprosium	Dy	66	162.500
Einsteinium	Es	99	[252]
Erbium	Er	68	167.259
Europium	Eu	63	151.964
Fermium	Fm	100	[257]
Fluorine	F	9	18.9984032
Francium	Fr	87	[223]
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.723
Germanium	Ge	32	72.64
Gold	Au	79	196.966569
Hafnium	Hf	72	178.49
Hassium	Hs	108	[270]
Helium	He	2	4.002602

(*Continued*)

TABLE 2.2 (*Continued*)
Symbols, Atomic Weights, and Atomic Numbers of the Elements

Element	Symbol	Atomic Number	Atomic Weight, a.m.u.[a]
Holmium	Ho	67	164.93032
Hydrogen	H	1	1.00794
Indium	In	49	114.818
Iodine	I	53	126.90447
Iridium	Ir	77	192.217
Iron	Fe	26	55.845
Krypton	Kr	36	83.798
Lanthanum	La	57	138.90547
Lawrencium	Lr	103	[262]
Lead	Pb	82	207.2
Lithium	Li	3	6.941
Lutetium	Lu	71	174.9668
Magnesium	Mg	12	24.3050
Manganese	Mn	25	54.938045
Meitnerium	Mt	109	[276]
Mendelevium	Md	101	[258]
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.96
Neodymium	Nd	60	144.242
Neon	Ne	10	20.1797
Neptunium	Np	93	[237]
Nickel	Ni	28	58.6934
Niobium	Nb	41	92.90638
Nitrogen	N	7	14.0067
Nobelium	No	102	[259]
Osmium	Os	76	190.23
Oxygen	O	8	15.9994
Palladium	Pd	46	106.42
Phosphorus	P	15	30.973762
Platinum	Pt	78	195.084
Plutonium	Pu	94	[244]
Polonium	Po	84	[209]
Potassium	K	19	39.0983
Praseodymium	Pr	59	140.90765
Promethium	Pm	61	[145]
Protactinium	Pa	91	231.03588
Radium	Ra	88	[226]
Radon	Rn	86	[222]
Rhenium	Re	75	186.207
Rhodium	Rh	45	102.90550
Roentgenium	Rg	111	[280]

(*Continued*)

TABLE 2.2 (*Continued*)
Symbols, Atomic Weights, and Atomic Numbers of the Elements

Element	Symbol	Atomic Number	Atomic Weight, a.m.u.[a]
Rubidium	Rb	37	85.4678
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	[267]
Samarium	Sm	62	150.36
Scandium	Sc	21	44.955912
Seaborgium	Sg	106	[271]
Selenium	Se	34	78.96
Silicon	Si	14	28.0855
Silver	Ag	47	107.8682
Sodium	Na	11	22.98976928
Strontium	Sr	38	87.62
Sulfur	S	16	32.065
Tantalum	Ta	73	180.94788
Technetium	Tc	43	[98]
Tellurium	Te	52	127.60
Terbium	Tb	65	158.92535
Thallium	Tl	81	204.3833
Thorium	Th	90	232.03806
Thulium	Tm	69	168.93421
Tin	Sn	50	118.710
Titanium	Ti	22	47.867
Tungsten	W	74	183.84
Ununbium[c]	Uub	112	[285]
Ununhexium	Uuh	116	[293]
Ununoctium	Uuo	118	[294]
Ununpentium	Uup	115	[288]
Ununquadium	Uuq	114	[289]
Ununtrium	Uut	113	[284]
Uranium	U	92	238.02891
Vanadium	V	23	50.9415
Xenon	Xe	54	131.293
Ytterbium	Yb	70	173.054
Yttrium	Y	39	88.90585
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.224

This table is based on the 2005 table in *Pure Appl. Chem.*, **78**, 2051–2066 (2006).

[a] a.m.u. = atomic mass unit, where 1 a.m.u. = 1.66×10^{-24}g.

[b] Values enclosed in brackets are the mass number for the longest-lived isotope.

[c] Elements 112–118 were under review when the information from the academic journal *Pure and Applied Chemistry* published this technical information. They have since been named.

regions in space where they possess the lowest possible energy—close to the nucleus but away from other negatively charged electrons. As electrons are placed into an atom, energy levels close to the positive nucleus are occupied first, and the higher energy levels are then successively populated. Extra stability appears to be associated with completely filled levels, termed "shells." Elements with completely filled shells include helium (atomic number 2), neon (atomic number 10), argon (atomic number 18), and krypton (atomic number 36). These elements all belong to a group called the "inert gases," and their virtual lack of any chemical reactivity provides support for the theory of filled-shell stability—the atoms do not wish to gain, lose, or share electrons.

Other elements show varying tendencies to obtain a filled shell by the sharing of electrons with other atoms or by the actual gain or loss of electrons to form charged species, called *ions*. For example, sodium (symbol Na, atomic number 11) readily loses one electron to form the sodium ion, Na^+, with ten electrons. By losing one electron, sodium has acquired the same number of electrons as the inert gas neon and it has become a very stable chemical species. Fluorine (symbol F, atomic number 9) readily acquires one additional electron to become the fluoride ion, F^-. This is another ten-electron species and is quite stable. Other elements display similar tendencies to gain or lose electrons to acquire "inert gas" electron configurations by becoming positive or negative ions. Many chemical species found in nature are *ionic compounds*. These are usually found as crystalline solids composed of interpenetrating lattices of positive and negative ions held together by electrostatic attraction between these oppositely charged particles. Table salt, or sodium chloride, is an ionic compound consisting of sodium and chloride ions, Na^+ and Cl^-, and one uses the formula NaCl to represent the one-to-one ionic ratio. The attractive forces holding the solid together are called *ionic bonds*.

Hence, if one brings together a good electron donor (such as a sodium atom) and a good electron acceptor (such as a fluorine atom), one might expect a chemical reaction to occur. Electrons are transferred and an ionic compound (sodium fluoride, NaF) is produced. A three-dimensional solid lattice of sodium and fluoride ions is created, where each sodium ion is surrounded by fluoride ions, and each fluoride ion is in turn surrounded by sodium ions. Another very important aspect of such a relation is the fact that *energy* is released as the product is formed. This release of energy associated with the formation of the reaction products becomes very important in the consideration of the chemistry of pyrotechnics and explosives.

In addition to forming ions by electron transfer, atoms may *share* electrons with other atoms as a means of acquiring filled shells (and their associated stability). The simplest illustration of this is the combination of two hydrogen atoms (symbol H, atomic number 1) to form a hydrogen *molecule*.

$$\mathrm{H} + \mathrm{H} \rightarrow \mathrm{H{-}H}\left(\mathrm{H_2}, \text{a hydrogen molecule}\right) \tag{2.1}$$

The sharing of electrons between two atoms is called a *covalent bond*. Such bonds owe their stability to the interaction of the shared electrons with *both* positive nuclei. The nuclei will be separated by a certain distance—termed the *bond distance*—that maximizes the nuclear–electron attractions balanced against the nuclear–nuclear repulsive forces. A *molecule* is a neutral species of two or more atoms held together by covalent bonds.

The element *carbon* (atomic number 6, symbol C) is almost always found in nature covalently bonded to other carbon atoms or to a variety of other elements (most commonly H, O, and N). Due to the presence of carbon-containing compounds in all living things, the chemistry of carbon compounds is known as *organic chemistry*.[2] Most high explosives are organic compounds. TNT (trinitrotoluene), for example, consists of C, H, N, and O atoms, with a molecular formula of $C_7H_5N_3O_6$. When TNT detonates, it produces a mixture of stable, small molecules such as N_2, CO_2, and H_2O as reaction products. We will encounter other organic compounds in our study of fuels and binders in energetic mixtures.

Covalent bonds can also form between dissimilar elements, such as hydrogen and chlorine:

$$\mathrm{H} + \mathrm{Cl} \rightarrow \mathrm{H{—}Cl}\left(\text{hydrogen chloride}\right) \tag{2.2}$$

By this combination, both atoms now have "filled-shell" electronic configurations and a hydrogen chloride molecule is formed. The sharing here is not exactly equal, however, for chlorine is a stronger electron attractor than hydrogen. The chlorine end of the molecule is slightly electron rich; the hydrogen end is electron deficient. This behavior can be noted using the Greek lowercase letter "delta", ∂, used as the symbol for "partial," as in

$$\overset{\partial+}{\mathrm{H}}{—}\overset{\partial-}{\mathrm{Cl}}$$

The bond that is formed in hydrogen chloride is termed *polar covalent*, and a molecule possessing these partial charges is referred to as "polar," since it has positive and negative "poles." The relative ability of atoms of different elements to attract electron density is indicated by the property termed *electronegativity*. A scale ranking the elements was developed by Nobel Laureate Linus Pauling. The electronegativity sequence for some of the more common covalent-bond forming elements is given in Table 2.3. Using this sequence, one can assign partial charges to atoms in a variety of molecules; the more electronegative atom in a given bond will bear the partial negative charge, leaving the other atom with a partial positive charge.

$$\overset{\partial-}{\mathrm{F}}{—}\overset{\partial+}{\mathrm{H}} \qquad \overset{\partial-}{\mathrm{N}}{—}\overset{\partial+}{\mathrm{I}} \qquad \overset{\partial-}{\mathrm{O}}{—}\overset{\partial+}{\mathrm{C}}$$

---

[2] "Organic" in chemistry terminology means carbon-based compounds; in biology terms, organic are those things that relate to an "organism" or living entity; and in farming/food products, it means those products are meeting certain standards of growth and processing. Numerous other meanings exist in business, law, and philosophy, to name a few.

TABLE 2.3
Electronegativity Values for Some Common Elements

Element	Pauling Electronegativity Value[a]
Fluorine, F	4.0
Oxygen, O	3.5
Nitrogen, N	3.0
Chlorine, Cl	3.0
Bromine, Br	2.8
Carbon, C	2.5
Sulfur, S	2.5
Iodine, I	2.5
Phosphorous, P	2.1
Hydrogen, H	2.1

[a] Pauling 1960.

TABLE 2.4
Boiling Points of Several Small Molecules

Compound	Formula	Boiling Point (°C at 1 atmosphere pressure)
Methane	CH_4	−164
Carbon dioxide	CO_2	−78.6
Hydrogen sulfide	H_2S	−60.7
Water	H_2O	+100

These partial charges, or dipoles, can lead to intermolecular attractions that play an important role in such physical properties as melting point and boiling point, and they are quite important in determining solubility as well. The boiling point of water, 100°C, is quite high when compared to values of other small molecules, as shown in Table 2.4. The high boiling point of water can be attributed to strong intermolecular attractions (called "dipole–dipole interactions") of the type shown in Figure 2.1.

The considerable solubility of polar molecules and many ionic compounds in water can be explained by dipole–dipole or ion–dipole interactions between dissolved species and the solvent, water, as shown in Figure 2.2.

The degree of solubility of solid compounds in water, as well as in other solvents, is determined by the competition between attractions in the solid state between molecules

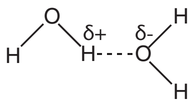

FIGURE 2.1 Intermolecular attractions (dipole–dipole interactions) of water. Note that the partially positive hydrogen atoms are attracted to the partially negative oxygen atoms (opposites attract).

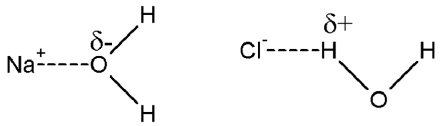

FIGURE 2.2 Dipole–dipole interactions between water and solvated NaCl (sodium chloride, or table salt). Note that the positive sodium ion is attracted to the partially negative oxygen atom, and the negative chloride ion is attracted to the partially positive hydrogen atom.

or ions and the solute–solvent attractions that occur in solution. A solid that is more attracted to itself than to the solvent molecules will not dissolve. A general rule of solubility is "likes dissolve likes"—a polar solvent such as water is most effective as dissolving polar molecules (such as sugar) and ionic compounds. A non-polar solvent such as gasoline is most effective at dissolving other non-polar species such as motor oil but it is a poor solvent for ionic species such as sodium chloride or potassium nitrate.

THE MOLE CONCEPT

Out of the atomic theory developed by John Dalton and other chemistry pioneers in the 19th century grew a number of important concepts essential to an understanding of all areas of chemistry, including pyrotechnics and explosives. The basic features of the atomic theory are:

1. The atom is the fundamental building block of matter and consists of positive, negative, and neutral subatomic particles. Approximately 90 naturally-occurring elements are known to exist (additional elements have been synthesized in the 20th and 21st centuries in the laboratory using high-energy nuclear reactions, but these unstable species are not found in nature).
2. Elements may combine to form more complex species called *compounds*. The *molecule* is the fundamental unit of a compound and consists of two or more atoms joined together by chemical bonds.
3. All atoms of the same element are identical in terms of the number of protons and electrons contained in the neutral species. Atoms of the same element may vary in the number of neutrons and therefore may vary in mass.
4. The chemical reactivity of an atom depends on the number of electrons; therefore, the reactivity of all atoms of a given element should be the same, and reproducible, anywhere in the world.
5. Chemical reactions consist of the combination or recombination of atoms, in fixed ratios, to produce new species.
6. A relative scale of atomic weights (as the weighted average of all forms, or isotopes, of a particular element found in nature) has been developed. The base of this scale is the assignment of a mass of 12.0000 to the isotope of carbon containing six protons, six neutrons, and six electrons. An atomic weight table can be found in Table 2.2.
7. As electrons are placed into atoms, they successively occupy higher energy levels or shells. Electrons in filled levels are unimportant as far as chemical reactivity is concerned. It is the outer, partially filled level that determines

> chemical behavior. Hence, elements with the same outer-shell configuration display markedly similar chemical reactivity. This phenomenon is called *periodicity*, and an arrangement the elements placing similar elements in a vertical column has been developed—the *periodic table*. The alkali metals (lithium, sodium, potassium, rubidium, and cesium) are one family of the periodic table—they all have one reactive electron in their outer shell. The halogens (fluorine, chlorine, bromine, and iodine) are another common family—they all have seven electrons in their outer shell and readily accept an eighth electron to form a filled level.

The mass of one atom of any element is infinitesimal and is impossible to measure on any existing balance. A more convenient mass unit was needed for laboratory work, and the concept of the *mole* emerged, where 1 mole (abbreviated in scientific notation as "1 mol") of an element is a quantity equal to the atomic weight in grams. One mole of carbon, for example, is 12.01 g, and 1 mol of iron is 55.85 g. The actual number of atoms in 1 mol of an element has been determined by several elegant experimental procedures to be 6.02×10^{23}. This quantity is known as *Avogadro's Number*, in honor of one of the pioneers of atomic theory. One can then see that 1 mol of carbon atoms (12.01 g) will contain exactly the same number of atoms as 1 mol (55.85 g) of iron. Using the mole concept, the chemist can now go into the laboratory and weigh out equal quantities of atoms of various elements.

The same concept holds for molecules. One mole of water (H_2O) consists of 6.02×10^{23} molecules and has a mass of 18.0 g. It contains 1 mol of oxygen atoms and 2 mol of hydrogen atoms covalently bonded to make water molecules. The *molecular weight* of a compound is the sum of the respective atomic weights, taking into account the number of atoms of each element that comprises the molecule. For ionic compounds, a similar concept termed *formula weight* is used. The formula weight of sodium nitrate, $NaNO_3$, is therefore:

$$\mathrm{Na} + \mathrm{N} + 3\mathrm{O's} = 23.0 + 14.0 + 3(16.0) = 85.0\ \mathrm{g/mol} \tag{2.3}$$

These concepts permit the chemist to examine chemical reactions and determine the mass relationships that are involved. For example, consider the simple pyrotechnic reaction

$$\begin{array}{lllllll} \mathrm{KClO_4} & + & 4\,\mathrm{Mg} & \rightarrow & \mathrm{KCl} & + & 4\mathrm{MgO} \\ 1\,\mathrm{mol} & & 4\,\mathrm{mol} & & 1\,\mathrm{mol} & & 4\,\mathrm{mol} \\ 138.6\,\mathrm{g} & & 97.2\,\mathrm{g} & & 74.6\,\mathrm{g} & & 161.2\,\mathrm{g} \end{array} \tag{2.4}$$

In a balanced chemical equation, the number of atoms of each element on the left-hand, or reactant, side will equal the number of atoms of each element on the right-hand, or product, side. The above equation states that 1 mol of potassium perchlorate ($KClO_4$) will react with 4 mol of magnesium metal to produce 1 mol of potassium chloride (KCl) and 4 mol of magnesium oxide (MgO). The potassium perchlorate and magnesium are called *reactants* since they "react" with one another, and the potassium chloride and magnesium oxide are *products* since they are the ones produced in the reaction.

In mass terms, 138.6 g (or pounds, tons, etc.) of potassium perchlorate will react with 97.2 g (or any other equivalent mass unit) of magnesium to produce 74.6 g of KCl and 161.2 g of MgO. This mass ratio will always be maintained regardless of the quantities of starting material involved. If 138.6 g (1.00 mol) of $KClO_4$ and 48.6 g (2.00 mol) of magnesium are mixed and ignited, only 69.3 g (0.50 mol) of the $KClO_4$ will react, completely depleting the magnesium. Remaining as "excess" starting material will be 0.50 mol (69.3 g) of $KClO_4^-$ there is no magnesium left for it to react with. The products formed in this example would be 37.3 g (0.50 mol) of KCl and 80.6 g (2.00 mol) of MgO, plus the 69.3 g of excess $KClO_4$.

The preceding example also illustrates the *law of conservation of mass*. In any normal chemical reaction (excluding nuclear reactions[3]), the mass of the starting materials will always equal the mass of the products (including the mass of any excess reactant). For example, 200 g of $KClO_4$/Mg mixture will produce 200 g of products (which includes any excess starting material).

The "formula" for the preceding illustration involved $KClO_4$ and Mg in a 138.6–97.2 mass ratio. The balanced mixture—with neither material present in excess—should then be 58.8% $KClO_4$ and 41.2% Mg by weight. The study of chemical weight relationships of this type is referred to as stoichiometry. A mixture containing exactly the quantities of each starting material corresponding to the balanced chemical equation is referred to as a *stoichiometric mixture*. Such balanced compositions are frequently associated with maximum performance in high-energy chemistry and will be referred to from time to time in subsequent chapters.

ELECTRON TRANSFER REACTIONS

OXIDATION–REDUCTION THEORY

A major class of chemical reactions involves the transfer of one or more electrons from one species to another. This process is referred to as an electron-transfer or *oxidation–reduction* reaction, or "redox reaction" (pronounced REE-dahks), where the species undergoing electron loss is said to be *oxidized*, while the species acquiring electrons is *reduced*. Pyrotechnics, propellants, and explosives belong to this chemical reaction category.

The determination of whether a species has undergone a loss or gain of electrons during a chemical reaction can be made out by assigning "oxidation numbers" to the atoms of the various reacting species and products, according to the following simple rules:

1. Except in a few rare cases, hydrogen is always +1 and oxygen is always −2. Metal hydrides and peroxides are the most common exceptions. This rule is applied first—it has highest priority, and the rest are applied in decreasing priority.

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[3] In nuclear reactions, mass is converted to energy, noting Einstein's famous relativity equation $E = mc^2$, where the energy output is equal to the mass being converted multiplied by the square of the speed of light.

2. Simple ions have their charge as their oxidation number. For example,

$$Na^+ \text{ is } +1,\ Cl^- \text{ is } 1,\ Al^{3+} \text{ is } +3, \text{ etc.}$$

The oxidation number of an element in its standard state—either as a monatomic atom such as metallic iron, Fe, or combined with itself to form a diatomic molecule, as in N_2 or O_2—is 0.

3. In a polar covalent molecule, the more electronegative atom in a bonded pair is assigned all of the electrons shared between the two atoms. For example, in H–Cl, the chlorine atom is assigned both bonded electrons making it identical to Cl and giving it an oxidation number of –1. The hydrogen atom therefore has an oxidation number of +1 (in agreement with rule #1 as well).
4. In a neutral molecule, the sum of the oxidation numbers will be 0. For an ion, the sum of the oxidation numbers on all the atoms will equal the net charge of the ion.

Examples

NH_3 (ammonia): The three hydrogen atoms are all +1 by rule 1. The nitrogen atom will therefore be –3 by rule number 4.

CO_3^{2-} (the carbonate ion): The three oxygen atoms are all –2 by rule 1. Since the ion has a net charge of –2, the oxidation number of carbon will be $3(-2) + x = -2$, $x = +4$ by rule 4.

For the reaction

$$KClO4 + ?\,Mg \rightarrow KCl + ?\,MgO$$

the oxidation numbers on the various atoms are as follows:

$KClO_4$: This is an ionic compound, consisting of the potassium ion, K+, and the perchlorate ion, ClO_4^-. The oxidation number of potassium in K+ will be +1 by rule 2. In ClO_4^-, the four oxygen atoms are all –2, making chlorine atom +7, by rule 4.

Mg: Magnesium is present in elemental form as a reactant, making its oxidation number 0 by rule 2.

KCl: This is an ionic compound made up of K^+ and Cl^- ions, with respective oxidation numbers of +1 and –1 by rule 2.

MgO: This is another ionic compound. Oxygen will be –2 by rule 1, leaving the magnesium ion as +2.

Examining the various changes in oxidation number that occur as the reaction proceeds, one can see that potassium and oxygen are unchanged in going from reactants to products. Magnesium, however, undergoes a change from 0 to +2, corresponding to a loss of two electrons per atom—it has lost electrons, or been *oxidized*. Chlorine undergoes an oxidation number change from +7 to –1, or a *gain* of eight electrons per atom—it has been *reduced*. In a balanced oxidation–reduction reaction, the electrons lost must equal the electrons gained; therefore, four magnesium atoms (each losing two electrons) are required to reduce one chlorine atom from the +7 (as ClO_4^-) to −1 (as Cl^-) state. The equation is now balanced.

$$KClO_4 + 4Mg \rightarrow KCl + 4MgO \tag{2.5}$$

Similarly, the equation for the reaction between potassium nitrate and sulfur can be balanced if one assumes, or has determined by laboratory analysis, that the products are potassium oxide, sulfur dioxide, and nitrogen gas:

$$?KNO_3 + ?S \rightarrow ?K_2O + ?N_2 + ?SO_2 \tag{2.6}$$

Again, analysis of the oxidation numbers reveals that potassium and oxygen are unchanged, with values of +1 and −2, respectively, on both sides of the equation. Nitrogen changes from a value of +5 in the nitrate ion $\left(NO_3^-\right)$ to 0 in elemental/molecular form as N_2. Sulfur changes from 0 in elemental form to a value of +4 in SO_2. In this reaction, then, sulfur is oxidized and nitrogen is reduced. To balance the equation, four nitrogen atoms, each gaining five electrons, and five sulfur atoms, each losing four electrons, are required. This results in 20 electrons gained and 20 electrons lost—they are balanced. The balanced equation is therefore:

$$2KNO_3 + 5S \rightarrow 2K_2O + 2N_2 + 5SO_2 \tag{2.7}$$

The ratio by weight of potassium nitrate and sulfur corresponding to a balanced—or stoichiometric—mixture will be 4(101.1) = 404.4 g (4 mol) of KNO_3 and 5(32.1) = 160.5 g (5 mol) of sulfur. This equals 72% KNO_3 and 28% S by weight.

THE PYRO VALENCE METHOD: A SIMPLE YET POWERFUL TECHNIQUE

The ability to balance oxidation–reduction equations can be quite useful in working out weight ratios for mixtures that should theoretically yield optimum pyrotechnic or explosive performance. An understanding of the oxidation number concept discussed in the previous section is valuable because it provides insight into which elemental species are directly related to the gain and loss of electrons.

However, for the practicing pyrotechnic researcher, the ability to quickly balance oxidation–reduction equations (or oxidizer–fuel ratios) as well as the ability to rapidly determine if a given composition is oxidizer-rich, fuel-rich, or stoichiometric can be quite valuable. While it is quite likely that some pyrotechnic reactions occurring quite rapidly at high temperature will yield a complex mixture of reaction products, it is likely that one reaction pathway will account for a majority of the products, and this is usually the pathway that will yield the most stable reaction products. It is always possible to carry out a laboratory analysis of the reaction products to confirm that you have identified the primary reaction that is occurring between an oxidizer and a fuel.

It is possible to rapidly perform these types of calculations using a method based on oxidation numbers (valences) put forward by Jain (Jain 1987). The use of this "Pyro Valence Method" can be of great value in the analysis of a large variety of quantitative problems associated with explosive, propellant, and pyrotechnic systems.

The Pyro Valence approach is based on the concept of oxidation numbers but concentrates on the oxidation numbers of each element in its most-stable-product form. Each element in an energetic mixture is assigned a "valence," which is the most common oxidation number of that element as a reaction *product*. An initial assumption in the Pyro Valence approach is that each element will react to form its normal, or most stable, oxidation state as a reaction product. Hence, any nitrogen present in a reactant is assumed to form N_2. Any chlorine is assumed to form Cl^-, any magnesium will form Mg^{2+}, and it is initially assumed that all carbon atoms will go to CO_2 (as opposed to CO, carbon monoxide). Hydrogen will be present in reaction products as H^+, usually either as H_2O or HCl. The valences for these elements are therefore 0 for N (since the oxidation number of N in N_2 is 0), –1 for Cl, since the oxidation number of Cl as Cl^- is –1, +2 for Mg, and +4 for C going to CO_2, where C would have an oxidation number of +4. A list of "Pyro Valences" for common elements used in pyrotechnic materials is given in Table 2.5.

To continue with the Pyro Valence approach, you then add up all of the atomic valences for a chemical compound, to obtain the molecular or compound valence. $KClO_4$ will have a net valence of –8, obtained by adding up 4 Os at –2 each, 1 Cl at –1, and 1 K at +1 (since K remains K^+ on the product side, as KCl). Any species under the Pyro Valence system that has a net *negative* valence (such as $KClO_4$ at –8)

TABLE 2.5
Pyro Valences for Elements Used to Calculate Valence for a Molecule or Formula Unit of Ionic Compound or Polymer

Element	Pyro Valence	Assumed Product
Aluminum, Al	+3	Al_2O_3
Barium, B	+2	BaO
Boron, B	+3	B_2O_3
Calcium, Ca	+2	CaO
Carbon, C	+4	CO_2—Carbon dioxide (most common)
Carbon, C	+2	CO—carbon monoxide
Chlorine, Cl	–1	HCl, KCl, other metal chlorides
Chromium, Cr	+3	Cr_2O_3
Fluorine, F	–1	HF, MgF_2, other metal fluorides
Hydrogen, H	+1	H_2O
Iron, Fe (in oxidizer)	0	Fe
Iron, Fe (as a fuel)	+3	Fe_2O_3
Magnesium	+2	MgO
Nitrogen, N	0	N_2
Oxygen, O	–2	H_2O, metal oxides
Potassium, K	+1	K_2O, KCl
Silicon, Si	+4	SiO_2
Sulfur, S	+4	SO_2
Titanium, Ti	+4	TiO_2
Zirconium, Zr	+4	ZrO_2

will have *oxidizing* ability—it has one or more elements in the compound that want to gain electrons (the Cl atom in $KClO_4$ for example). A list of net valences for some of the common oxidizers is given in Table 2.6.

Similarly, any species with a net positive Pyro Valence has *reducing* ability or is a fuel. A metal fuel such as aluminum (Al) will have a valence of +3, since it will lose three electrons to produce Al^{3+} product (usually in the form of Al_2O_3). An organic compound such as a simple sugar, with formula $C_6H_{12}O_6$ will have a net valence of 6(+4) + 12(+1) + 6(–2) for the C, H, and O atoms that are present. This adds up to a net of +24, indicating that sugar—even though it contains six oxygen atoms per molecule—is still a net fuel. Net Pyro Valences for some common fuels and explosive compounds are given in Table 2.7.

TABLE 2.6
"Pyro Valences" for Some Common Pyrotechnic Oxidizers

Oxidizers	Valence	Products
Potassium nitrate, KNO_3	–5	K_2O, N_2, oxide/fuel
Potassium perchlorate, $KClO_4$	–8	KCl, oxide/fuel
Potassium chlorate, $KClO_3$	–6	KCl, oxide/fuel
Ammonium perchlorate, NH_4ClO_4	–5	N_2, H_2O, HCl, oxide
Barium nitrate, $Ba(NO_3)_2$	–10	BaO, N_2, oxide/fuel
Iron(III) oxide, Fe_2O_3	–6	Fe, oxide/fuel
Barium chromate, $BaCrO_4$	–3	BaO, Cr_2O_3, oxide
Red lead oxide, Pb_3O_4	–8	Pb (valence = –2 if PbO is formed)
Ammonium nitrate, NH_4NO_3	–2	N_2, H_2O, oxide

TABLE 2.7
Pyro Valences of Some Common Fuels & Explosives

Compound	Valence	Reaction Products
Fuel Oil, –(CH_2–CH_2)– (unit mass = 28 g/mol)	+12 per unit	CO_2, H_2O
Glucose, $C_6H_{12}O_6$	+24	CO_2, H_2O
Polyvinyl Chloride, –(CH_2–CHCl)– (unit mass = 62.5 g/mol)	+10 per unit	CO_2, HCl, H_2O
TNT, $C_7H_5N_3O_6$	+21	CO_2, H_2O, N_2
RDX, $C_3H_6N_6O_6$	+6	CO_2, H_2O, N_2
EGDN, ethylene glycol dinitrate, $C_2H_4N_2O_6$	0! (stoichiometric)	CO_2, H_2O, N_2
Nitroglycerine, $C_3H_5N_3O_9$	–1 (O-rich)	CO_2, H_2O, N_2
Sodium azide, NaN_3	0	Na, N_2 (extra energy can be obtained if the sodium metal product is oxidized to Na^+ by an oxidizer)

Note: Some elemental fuels may be found in the Table of Elements.

Once Pyro Valences have been assigned to all reactant species, we can proceed to balance an equation by the use of the concept that in a balanced equation, the sum of the oxidizing valences will equal the sum of the reducing valences, and the net, overall valence will be zero. This is the equivalent of saying that the number of electrons lost will equal the number of electrons gained—electrons are neither created nor destroyed in these reactions, they just move from one atomic species to another during a chemical reaction.

For example, consider ammonium perchlorate: NH_4ClO_4

$$\text{Total valence} = \underset{\text{N}}{0} + \underset{\text{4H's}}{4(+1)} + \underset{\text{Cl}}{(-1)} + \underset{\text{4O's}}{4(-2)} = -5$$

Since the total valence is a net negative value (–5), ammonium perchlorate will be an oxidizing species.

Now, let us look at a simple sugar such as glucose: $C_6H_{12}O_6$

$$\text{Total valence} = \underset{\text{6C's}}{6(+4)} + \underset{\text{12H's}}{12(+1)} + \underset{\text{6O's}}{6(-2)} = +24$$

Since the net molecular Pyro Valence is positive, glucose will be a fuel.

And suppose you then wanted to balance the equation for the reaction between glucose and ammonium perchlorate. The key to balancing an equation by the Pyro Valence Method is to remember that the oxidizing valences will equal the reducing valences or the sum of the valences will equal zero.

BALANCING AN EQUATION

To balance an energetic equation, determine the coefficients (smallest whole number ratio) that will produce equal valences.

For ammonium perchlorate, or AP (–5) and glucose (+24), you will need 24 APs and five glucoses in the balanced equation. There are no smaller factors for the numbers 24 and 5. Put these coefficients in for the reactants, and you have balanced the equation. You can then work out how many moles of each product will form, if you so desire.

$$24NH_4ClO_4 + 5C_6H_{12}O_6 \rightarrow 30CO_2 + 66H_2O + 12N_2 + 24HCl \tag{2.8}$$

Note: This method assumes that all N winds up as N_2 and all Cl winds up as HCl.

All the C atoms in the fuel are assumed to go to CO_2, all the H atoms go to H_2O or HCl and all the N atoms become N_2. Upon inspection, the equation is balanced.

Note: The Pyro Valence method works equally well if one wishes to calculate the stoichiometric mixture for a composition where carbon monoxide (CO) is the assumed product formed by the carbon atoms in the fuel. To do this, use +2 as the valence for carbon in the calculations, and the net valence for glucose will be +12. The balanced equation will be

$$12NH_4ClO_4 + 5C_6H_{12}O_6 \rightarrow 30CO + 48H_2O + 6N_2 + 12HCl \tag{2.9}$$

IS A CHEMICAL COMPOUND FUEL OR OXYGEN RICH?

The Pyro Valence procedure also provides a very easy way to calculate if a specific molecule or compound is fuel rich, oxygen rich, or stoichiometric. Consider, for example, the compound trinitrotoluene, better known as TNT, with a molecular formula of $C_7H_5N_3O_6$. TNT is a powerful explosive, but is it oxygen-balanced? The Pyro Valence method provides an easy, quick way to tell. Simply add up the atomic valences multiplied by the number of atoms of each element found in the molecule:

$$\text{TNT's Pyro Valence} = 7(+4) + 5(+1) + 3(0) + 6(-2) = +21$$

7 C's 5 H's 3 N's 6 O's

Because of the large, positive valence, we can see that TNT is a very fuel-rich explosive—more energy should theoretically be obtainable if TNT is combined with an oxygen-rich explosive, to better utilize TNT's fuel capacity. When TNT is detonated by itself, a large cloud of dark smoke is produced, due to a significant amount of atomic carbon being formed instead of all of the carbon being oxidized to carbon dioxide, CO_2. In theory, then, we would expect a candidate molecular explosive that has a significant number of positive and negative valences that add up close to zero to be of great interest.

The molecular nitramine explosive HMX with molecular formula $C_4H_8N_8O_8$ has a positive valence total of +24 (4 Cs and 8 Hs) and a negative valence total of –16 (8 Os), for a net molecule valence of +8 (fuel rich). If carbon monoxide (CO) is the product from the carbons however, we have valences of +16 and –16, for a molecule Pyro Valence of *zero*. Perhaps this has something to do with the high-detonation velocity of HMX—over 9,000 m/s.

What about methylammonium perchlorate, $CH_3NH_3ClO_4$?

Ammonium perchlorate, NH_4ClO_4, is a good oxidizer, with a Pyro Valence of –5. A similar compound, methylammonium perchlorate might be considered for use in energetic mixtures as well, and it might be assumed initially that methylammonium perchlorate (or MAP) will also serve as an oxidizer. However, the replacement of an H atom by a CH_3 group has significantly altered the nature of the compound, as shown in the valence calculation:

$$\text{Valence} = 1(+4) + 6(+1) + 0 + 1(-1) + 4(-2) = -1 \ (\text{a net fuel!})$$

1 C 6 H's 1 N 1 Cl 4 O's

The calculation shows that the compound is actually now slightly *fuel-rich* and very close to stoichiometric. If you combined MAP with a fuel, hoping to get a violent reaction, you would probably be disappointed—MAP is already fuel-rich with carbon dioxide as the product.

A logical question to ask at this point is: Are there any energetic compounds that are actually internally stoichiometric going to CO_2 as the carbon product or have a net valence of 0? What about ethylene glycol dinitrate, or EGDN—a material used in many dynamites for low temperature applications? EGDN has a molecular formula of $C_2H_4N_2O_6$. Its Pyro Valence will be:

$$2(+4)+4(+1)+2(0)+6(-2)=0-\text{a stoichiometric explosive going to } CO_2!$$

In actual practice, EGDN is a good explosive, but it does not rise dramatically above other explosives in terms of its performance. Its net valence of 0 is as much a chemical curiosity as anything; other explosives are capable of very rapid, energetic reactions even if they deviate somewhat from internal stoichiometry. If you wish to enhance the performance of an explosive compound, however, the ideal material to add would be an oxidizer or a fuel—whichever one will bring the overall system closer to oxygen balance.

WEIGHT RATIO CALCULATIONS

The Pyro Valence approach provides a simple procedure for calculating the weight of any fuel needed to react with a given oxidizer in stoichiometric proportions. The ammonium nitrate/fuel oil system (or "ANFO"), widely used as a commercial blasting agent, provides a good example. We will assume that fuel oil can be represented by CH_2, which is the repeating unit that makes up the vast majority of a fuel oil molecule.

The valence for ammonium nitrate (NH_4NO_3) is

$$2(0)+4(+1)+3(-2)=-2(\text{oxidizer})$$

The valence for a hydrocarbon unit (CH_2) is

$$(+4)+2(+1)=+6(\text{fuel})\big(\text{per } 14\,\text{g or } 1\,CH_2\text{unit}\big)$$

The balanced equation will therefore require 3 ANs for each CH_2unit by the valence method, or

	$3NH_4NO_3$	+	CH_2	→	CO_2	+	$7H_2O$	+	$3N_2$
Mass:	3(80)		14						

Ammonium nitrate has a formula weight of 80, while the CH_2 fragment has a mass of 14. The mass ratio for the above balanced equation is therefore,

$$3(80):14=240:14,\text{ or } 94.5:5.5$$

which is almost the exact ratio found in the ANFO explosives. This ratio (the stoichiometric ratio) maximizes the energy output from the system by fully utilizing all the available oxygen and all the available fuel.

Note: It is highly likely that a pyrotechnic reaction will yield more than a single set of reaction products, due to the possibility of multiple reactions occurring and competing at high-reaction temperatures and very fast reaction rates. The thermodynamically favored reaction will have competition from other reaction pathways, but the stoichiometry that is predicted using the Pyro Valence approach represents a good starting point in the development of a new formulation.

Once the initial composition has been prepared and its reaction rate measured, vary the oxidizer/fuel ratio up and down in small increments and observe the effect on the reaction rate. This will give you both an insight into the effect of small changes in composition on the reactivity of the composition as well as an indication of whether you are close to the actual stoichiometric point for the primary reaction that is occurring when the test material is ignited.

Remember, you can always perform a chemical analysis of the reaction products to verify if your proposed primary reaction is, in fact, the one that is taking place. That is the beauty of chemistry—theory can usually be confirmed or disproved by a trip to the lab.

Analyzing the Pyro Valence of a Mixture

Analyzing a mixture by the Pyro Valence method consists of calculating the valence for a given *mass* (which is typically assumed to be 100 g for easier calculation purposes) of the mixed composition. This is accomplished by first calculating the number of *moles* of each component in 100 g of the mixture, using the molecular or formula weight of each component. The actual number of moles of each species in 100 g is then multiplied by the appropriate pyro valence to calculate the fractional valence for each component. These individual valences are then summed up to give the net valence for 100 g of composition. If this sum is negative, the mixture is oxygen rich; if it is positive, the composition is fuel rich; and if the net valence is 0, the mixture is stoichiometric.

Consider an 80:20 mixture (by weight) of potassium perchlorate and titanium ($KClO_4$/Ti). Assume that you have 100 g for calculation purposes. You do not need to balance the equation to perform this analysis.

	$KClO_4$	+	**Ti**	→	**KCl**	+	**TiO_2**
M, Mass (g):	80		20				
FW, Formula weight (g/mol):	138.6		47.9				
# Moles (M/FW):	0.577		0.418				
Valence (per FW):	−8		+4				
Fractional valence (mol × valence):	−4.62		+1.67				

$$\text{Sum}\left(\text{KP fractional valence} + \text{Ti fractional valence}\right) = -2.95$$

The sum of the Pyro Valences in this mixture is −2.95; therefore, this mixture is oxidizer-rich and the addition of more titanium should yield an even-more-reactive formulation. If the valences had added up to zero, the mix would have been stoichiometric.

Three-Component Systems

The analysis is essentially identical for systems with more than two components and provides a very simple means of determining the oxygen balance of more complex mixtures. Again, the one assumption that must be made involves what reaction products will form, for this determines the Pyro Valence of each reacting element. Once this has been done, calculate the number of moles of each component in 100 g of mix, calculate the valences for each component, and see if the sum is negative (oxidizer-rich) or positive (fuel-rich). In this example, we will use polymethylmethacrylate (PMMA) as a fuel/binder. PMMA is a polymer consisting of a chain of $C_5H_8O_2$ units; calculations for polymers can be performed on the monomer unit, since the use of the appropriate formula weight cancels out any discrepancy and greatly simplifies calculations with polymers. Let us analyze a mixture that is 60/35/5 $KClO_4$/Ti/PMMA by weight.

	$KClO_4$	+	Ti	+	$C_5H_8O_2$	$\rightarrow KCl + CO_2 + H_2O + TiO_2$
Weight	60		35		5	Grams per 100g of mixture
FW	138.5		47.9		100	Grams per mole
Moles	0.433		0.731		0.050	Grams/formula weight
Valence/mole	−8		+4		+24	Valence of each species
Valence/formula	−3.46		+2.92		+1.20	# moles × valence/mole

$$\text{Sum} = +0.66\left(\text{mixture is fuel-rich}\right)$$

There is just no easier way to analyze complex mixtures to determine if they are oxidizer-rich, fuel-rich, or stoichiometric. While there are computer programs that can perform detailed calculations on energetic mixtures, the Pyro Valence method gives you some quick insight into the fundamental nature of an energetic system and suggests the effect that various chemical additives might have on the system. Here are a few exercises using the Pyro Valence method:

PYRO VALENCE EXERCISES

1. Calculate the stoichiometric composition for the potassium perchlorate/aluminum system.

$$KClO_4 + Al \rightarrow KCl + Al_2O_3$$

2. Determine whether the following composition is fuel- or oxidizer-rich:

Potassium Perchlorate	Glucose	Polyvinyl chloride (PVC)
$KClO_4$	$C_6H_{12}O_6$	$-(C_2H_3Cl)-$
65	25	10 (parts by wt.)

3. Develop the stoichiometric mixture for potassium perchlorate/glucose/PVC for a composition that contains 5% PVC by weight.
4. A delay system consisting of barium chromate ($BaCrO_4$), potassium perchlorate ($KClO_4$), and molybdenum (Mo) is desired containing 10% $KClO_4$. What would be the stoichiometric mixture? Reaction products are assumed to be BaO, Cr_2O_3, KCl, and MoO_3.

5. Develop the stoichiometric ratio for the ammonium perchlorate (NH_4ClO_4)/ sucrose ($C_{12}H_{22}O_{11}$) system. The formula weight for AP is 117.5; the molecular weight of sucrose is 342.

Solutions and Answers to the Exercises

1. Complete the reaction:

$$KClO_4 + Al \rightarrow KCl + Al_2O_3\left(\text{expected products}\right)$$

Calculate/look up Pyro Valences of the oxidizer and fuel:

$$\begin{array}{ll} KClO_4 & V = +1-1+4(-2) = -8 \\ Al & V = +3 \end{array}$$

Balance oxidizer and fuel valences:

$$KClO_4 - 8 \times 3 = -24$$

$3KClO_4$s are needed to balance the valences of 8 Als

$$Al + 3 \times 8 = +24$$

So the balanced equation is:

$$\underline{3}KClO_4 + \underline{8}Al \rightarrow \underline{3}KCl + \underline{4}Al_2O_3$$

Note: 4 mol of Al_2O_3 contains 8 mol of aluminum atoms. The mass relationship is therefore:

$$\begin{array}{ll} 3KClO_4: & 8Al \\ 3(138.5): & 8(27)g \\ 415.5: & 216g \end{array}$$

The % $KClO_4$ in the stoichiometric (balanced) mix is:

$$\%KClO_4 = 415.5/(415.5 + 216) = .658 \times 100 = 65.8\%$$

The aluminum % is 216/(415.5 + 216) = 0.342 × 100 = 34.2%
Check: the sum of the percentages should equal 100%, if you have done everything right.

2. Is a composition fuel- or oxidizer-rich?

	$KClO_4$	$C_6H_{12}O_6$	$-(C_2H_3Cl)-$
A. Parts by weight	65	25	10
B. Formula weight	138.5	180	62.5 (per monomer unit)
C. # moles (A/B)	0.47	0.14	0.16
D. Pyro valence	−8	+24	+10
E. net valence (C × D)	−3.8	+3.3	+1.6

$$\text{Pyro Valence sum}\left(\text{net valence}\right) = +1.1\text{, so mix is } \underline{\text{fuel rich}}$$

3. Develop the stoichiometric mixture for potassium perchlorate/glucose/PVC that contains 5% PVC by weight. This problem gives you an opportunity to use that algebra you never thought you would need again.

   Let x = grams of glucose in 100 g of the mix. Since there are 5 g of PVC (5%), you will therefore have 95 – x grams of potassium perchlorate. The weights are therefore:

	$KClO_4$	**$C_6H_{12}O_6$**	**$-(C_2H_3Cl)-$**
Grams	$95 - x$	x	5
A. # moles	$95 - x/138.5$	$x/180$	5/62.5
B. Pyro valence	−8	+24	+10
C. Net valence (A × B)	$\frac{-8(95-x)}{138.5}$	$\frac{+24(x)}{180}$	$\frac{+10(5)}{62.5}$

   For a stoichiometric mix, the total valence = 0. Therefore:

$$\text{Valence}(KClO_4) + \text{Valence}(C_6H_{12}O_6) + \text{Valence}(PVC) = 0$$

   Set the sum of the net valences in (C) equal to 0 and solve for x.
   x = **24.5** = #grams of glucose in the stoichiometric mixture.
   Therefore, #grams of $KClO_4 = 95 - x = 95 - 24.5 =$ **70.5** g
   The balanced mixture is:

$KClO_4$	**Glucose**	**PVC**
70.5%	24.5%	5%

4. Molybdenum delay system, 10% $KClO_4$. Calculate the percentages in the stoichiometric mixture: First, let x = grams Mo in 100 g of mixture.

   The percentages (g/100 g) are:

	$BaCrO_4$	**$KClO_4$**	**Mo**
Grams	$90 - x$	10	X
A. Formula weight	253.3	138.5	95.9
B. Pyro valence	−3	−8	+6*
C. # Moles in mix	$\frac{90-x}{253.3}$	$\frac{10}{138.5}$	$\frac{x}{95.9}$
D. Net valence (B × C)			

   For a stoichiometric mix, the sum of all valences will = 0, so the sum of the entries in line D is set = 0:

$$-3\left(\frac{90-x}{253.3}\right) + -8\left(\frac{10}{138.5}\right) + 6\left(\frac{x}{95.9}\right) = 0$$

solve this equation for x (or get a ninth-grader taking algebra to work it out for you). You should get x = 22.1, which is the # grams of Mo in the stoichiometric mixture.

The stoichiometric mix is therefore:

$BaCrO_4$	$KClO_4$	Mo
67.9	10.0	22.1 (parts by weight)

*The Pyro Valence of Mo is obtained by analysis of the formula of the reaction product, MoO_3. Mo in this compound has an oxidation number of +6, and the valence is therefore +6 for Mo metal.

5. This one is about as messy as they get. The valence for ammonium perchlorate is +5 (oxidizer); the valence for sucrose is −48(−48 − 22 + 22). The balanced equation is therefore:

$$48NH_4ClO_4 + 5C_{12}H_{22}O_{11} \rightarrow 60CO_2 + 48HCl + 127H_2O + 24N_2$$

$$\begin{aligned} \text{Weights:} \quad & 48(117.5) : 5(342)\text{g} \\ & 5{,}640 : 1{,}710 \\ & 76.7\% : 23.3\% \text{ by weight} \end{aligned}$$

ADDITIONAL PYRO VALENCE PROBLEMS

1. A flare composition is 15% $KClO_4$, plus it contains strontium nitrate (a second oxidizer) and magnesium (fuel). What will be the composition of the stoichiometric mixture? Assume that $Sr(NO_3)_2$ forms SrO, N_2, and oxygen. The magnesium will form MgO, and $KClO_4$ will form KCl and oxygen (which combines with Mg and Sr).

   Answer: 15% $KClO_4$, 47.3% Sr(NO3)2, 37.7% Mg
2. A flare mixture contains 45% $Ba(NO_3)_2$, 35% Mg, and 20% polyvinyl chloride (PVC, C_2H_3Cl polymer). Is this mixture fuel-rich or fuel-lean?

   Answer: Net valences for 100 g are −1.72 for barium nitrate, +2.88 for Mg, and +3.20 for PVC. Sum of all valences is +4.36, so the mixture is fuel-rich.
3. Ferric oxide (Fe_2O_3) and boron (B) makes an interesting low-toxicity delay mixture. What is the composition of the stoichiometric mixture, assuming that the reaction products are Fe and B_2O_3? Valences are −6 for ferric oxide and +3 for boron.

   Answer: 88.1% Fe_2O_3, 11.9% B
4. Aluminized ammonium nitrate/fuel oil (aluminized ANFO) is a popular commercial explosive. If a mixture contains 5% Al by weight, what weights of ammonium nitrate (Valence = −2) and fuel oil will make up the stoichiometric mixture. Assume that ammonium nitrate forms N_2, 2 H_2O, and evolves 1 O atom per formula unit. Also assume that fuel oil can be represented by –CH2–with a molecular weight of 14 and a Valence of +6.

   Answer:

Begin	NH_4NO_3	Al	$-CH_2-$
Grams	$95 - x$	5	x

Stoichiometric mixture: Ammonium nitrate 91.0%, Al 5.0%, Fuel Oil 4.0%

ELECTROCHEMISTRY

If one takes a spontaneous electron-transfer reaction and *separates* the materials undergoing oxidation and reduction, a battery is created by allowing the electron transfer to occur through a good conductor, such as a copper wire. By proper design, electrical energy associated with reactions of this type can be harnessed. The fields of electrochemistry (e.g., batteries) and pyrotechnics (e.g., fireworks) are actually very close relatives. The reactions involved in the two areas can look strikingly similar:

$$Ag_2O + Zn \rightarrow 2Ag + ZnO\left(\text{a battery reaction}\right) \tag{2.10}$$

$$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3\left(\text{a pyrotechnic reaction}\right) \tag{2.11}$$

In both fields of research, one is looking for inexpensive, high-energy electron donors and acceptors that will readily yield their energy on demand yet be quite stable in storage.

It is interesting to note that many of the energetic materials used in the fields of explosives and pyrotechnics owe their high-energy potential to the use of electrochemistry in the manufacturing process. Through electrolysis or electrochemical processes, modern technology converts Mg^{2+} to Mg metal, and converts chloride ions (Cl^-) to ClO_3^- (chlorate) and ClO_4^- (perchlorate) by the passage of an electric current through molten material in a reaction vessel. We do not find these materials in any significant quantity in nature—any that might be created by lightning or other high-energy natural processes usually convert quickly to their lower-energy forms (Mg^{2+}, Cl^-) by electron transfer reactions with naturally occurring chemical species. Magnesium metal, for example, will react with water to form $Mg(OH)_2$ and hydrogen gas, H_2. Iron metal, formed from Fe^{3+} by a high-energy process in a blast furnace, all too quickly reverts to rust (Fe_2O_3) when exposed to air and moisture and even quicker if exposed to stronger oxidizers or acids.

Many high-energy explosive molecules such as nitroglycerine and trinitrotoluene (TNT) similarly owe their stored energy to electrochemical processes or the energy stored in these energetic species has its origin in solar and biochemical processes.

Therefore, in many ways, a pyrotechnic device is quite similar to a battery. Both provide packaged energy consisting of an electron donor and an electron acceptor. In a battery, we cause the energy contained within the chemical species to be released by closing a circuit and allowing a flow of electrons to occur, and work is performed in the process. With a pyrotechnic system, we intimately blend the electron donor and electron acceptor and require that an energy input (e.g., friction, impact, or the flame and sparks from a burning piece of fuse) be imposed on the system to initiate the electron transfer reaction. Once the reaction begins, it generates sufficient energy to become self-sustaining and no further external energy input (such as the flame from a fuse) is required.

Electrochemists have developed extensive tables listing the relative tendencies of materials to donate or accept electrons, and these tables can be quite useful to the pyrotechnic chemist in a search for new materials. Chemicals are listed in order of decreasing tendency to gain electrons and are all expressed as *half-reactions* in the reduction direction, with the half-reaction

$$H^+ + e^- \rightarrow \frac{1}{2}H_2 0.000\,V \tag{2.12}$$

arbitrarily assigned a value of 0.000 V (for volts), also called the "standard reduction potential." All other species are measured relative to this reaction, with more readily reducible species having positive voltages/standard reduction potentials, and less-readily reducible species showing negative voltages/standard reduction potentials. Species with sizeable negative potentials should then, logically, be the best electron *donors*, while species with sizeable positive potentials will be the best electron *acceptors*. (*Note:* this is the *opposite* for the Pyro Valence: an oxidizer will have a negative Pyro Valence but a positive standard reduction potential, while a fuel will have a positive Pyro Valence with a negative standard reduction potential.)

A combination of a good electron donor with a good electron acceptor should produce a battery of high voltage. Such a combination will also be a potential candidate for a pyrotechnic system. However, one must bear in mind that most of the values listed in the electrochemistry tables are for reactions in solution, rather than for solids, so direct calculations cannot be made for pyrotechnic systems. However, some good ideas for candidate materials can be obtained.

A variety of materials of pyrotechnic interest and their standard reduction potentials at 25°C are listed in Table 2.8. Note the large positive values associated with certain oxygen-rich negative ions, such as the chlorate ion $\left(ClO_3^-\right)$, and the large negative values associated with certain active metal fuels, such as aluminum (Al).

TABLE 2.8
Standard Reduction Potentials

Half-Reaction	**Standard Potential @25°C, in Volts**[a]
$F_2 + 2e^- \rightarrow 2F^-$	2.87
$CO_3^+ + e^- \rightarrow CO_2^+$	1.8
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4(s) + 2H_2O$	1.69
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.49
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H_+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23
$Br_2 + 2e^- \rightarrow 2Br^-$	1.07
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96
$Hg^{2+} + 2e^- \rightarrow Hg$	0.85
$Ag^+ + e^- \rightarrow Ag$	0.8
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77
$I_2 + 2e^- \rightarrow 2I^-$	0.54
$Cu^+ + e^- \rightarrow Cu$	0.52
$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$	0.36
$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Cu^{2+} + e^- \rightarrow Cu^+$	0.15
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	0.15

(*Continued*)

TABLE 2.8 (*Continued*)
Standard Reduction Potentials

Half-Reaction	Standard Potential @25°C, in Volts (West 1994)
$2H^+ + 2e^- \rightarrow H_2$	0
$Fe^{3+} + 3e^- \rightarrow Fe$	–0.04
$Pb^{2+} + 2e^- \rightarrow Pb$	–0.13
$Sn^{2+} + 2e^- \rightarrow Sn$	–0.14
$Ni^{2+} + 2e^- \rightarrow Ni$	–0.25
$CO^{2+} + 2e^- \rightarrow CO$	–0.29
$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	–0.359
$PbI_2 + 2e^- \rightarrow Pb + 2I^-$	–0.365
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	–0.4
$Cd^{2+} + 2e^- \rightarrow Cd$	–0.4
$Fe^{2+} + 2e^- \rightarrow Fe$	–0.41
$Cr^{3+} + 3e^- \rightarrow Cr$	–0.74
$Zn^{2+} + 2e^- \rightarrow Zn$	–0.76
$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$	–0.83
$V^{2+} + 2e^- \rightarrow V$	–1.18
$Mn^{2+} + 2e^- \rightarrow Mn$	–1.18
$Al^{3+} + 3e^- \rightarrow Al$	–1.66
$Mg^{2+} + 2e^- \rightarrow Mg$	–2.37

[a] West (1994).

THERMODYNAMICS

INTRODUCTION TO THERMODYNAMICS

There are a vast number of possible reactions that the chemist working in the explosives and pyrotechnics field can write between various electron donors (fuels) and electron acceptors (oxidizers). Whether a particular reaction will occur and thereby be of possible use depends on two major factors:

1. Whether or not the reaction is *spontaneous* or will actually occur if the oxidizer and fuel are mixed together.
2. The *rate* at which the reaction will proceed or the time required for complete reaction to occur.

Spontaneity is determined by a quantity known as the *free energy change*, ΔG. "Δ" is the symbol for the upper-case Greek letter "delta" and is used as the symbol for "change in." To put it another way, ΔG can be read as "change in free energy."

The thermodynamic requirement for a reaction to be spontaneous (at constant temperature and pressure) is that the products are of lower free energy than the reactants, or that ΔG—the change in free energy associated with the chemical reaction—be a negative value. Two quantities comprise the free energy of a system at a given temperature. The first is *enthalpy*, or heat content, represented by the symbol H. The second is the *entropy*, represented by the symbol S, which may be viewed as the randomness or disorder of the system. The free energy of a system, G, is equal to $H - TS$, where T is temperature of the system on the Kelvin, or absolute, scale. (To convert from Celsius to Kelvin temperature, add 273.15 to the Celsius degrees value.) The free energy change accompanying a chemical reaction at constant temperature is therefore given by[4]

$$\Delta G = G(\text{products}) - G(\text{reactants}) = \Delta H - T\Delta S \qquad (2.13)$$

For a chemical reaction to be spontaneous, or energetically favorable, it is desirable that ΔH, or the enthalpy change, be a negative value, corresponding to the liberation of heat (energy) by the reaction. Any chemical process that liberates heat is termed *exothermic*, while a process that absorbs heat is called *endothermic* ("exo" from the Greek for "outer," and "endo" from the Greek for "inner"). ΔH values for many high-energy reactions have been experimentally determined as well as theoretically calculated. The typical units for ΔH, or *heat of reaction*, are calories/mole or calories/gram. The International System of units (SI System) calls for energy values to be given in *joules*, where 1 calorie (cal) = 4.184 joules (J). Most thermochemical data acquired prior to the 1980s are found with the calorie as the unit, and it will be used in this book in most instances. Some typical ΔH values for pyrotechnics are given in Table 2.9.

TABLE 2.9
Typical ΔH Values for "High-Energy" Reactions

	Composition (% by Weight)	ΔH (kcal/g)[a]	Application
$KClO_4$	60	−2.24	Photoflash
Mg	40		
$NaNO_3$	60	−2.00	White Light
Al	40		
Fe_2O_3	75	−0.96	Thermite (heat)
Al	25		
KNO_3	75	−0.66	Black Powder
C	15		
S	10		
$KClO_3$	57	−0.61	Red Light
$SrCrO_3$	25		
Shellac	18		
$KClO_3$	35	−0.38	Red Smoke
Lactose	25		
Red dye	40		

[a] Shidlovskiy (1964). All values represent heat *released* by the reaction and are therefore shown as negative.

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[4] Only free energy, enthalpy, and entropy change and thus have the Δ next to them; recall that these are calculated at a constant temperature, and therefore there is no change in, or delta, temperature.

Note 1: 1 kcal = 1,000 cal.

Note 2: 1 cal = 4.184 J, for conversion purposes

It is also favorable to have the entropy change, ΔS, be a positive value, making the $-T\Delta S$ term in Equation 2.13 a negative value. A positive value for ΔS corresponds to an increase in the randomness or disorder of the system when the reaction occurs. The entropies of the various states of matter show the following trend:

$$S(\text{solid}) < S(\text{liquid}) \ll S(\text{gas})$$

Therefore, a process of the type "solids→gas" (common to many high-energy systems) is particularly favored by the change in entropy occurring upon reaction. Reactions that evolve heat *and* form gases from solid starting materials should be favored thermodynamically and fall in the "spontaneous" category. Chemical processes of this type will be discussed in subsequent chapters.

HEAT OF REACTION

It is possible to calculate a heat of reaction for a high-energy system by assuming what the reaction products will be and then using available thermodynamic tables of *heats of formation*. Heat of formation is the heat associated with the formation of a chemical compound from its constituent elements. For example, for the reaction

$$2\text{Al} + 3/2\,\text{O}_2 \rightarrow \text{Al}_2\text{O}_3 \tag{2.14}$$

ΔH is −400.5 kcal/mol of Al_2O_3, and this value is therefore the heat of formation (given by the symbol ΔH_f) of aluminum oxide (Al_2O_3). The reaction of 2.0 mol (54.0 g) of aluminum with 1.5 mol of oxygen gas (48.0 g) to form Al_2O_3 (1.0 mol, 102.0 g) will liberate 400.5 kcal of heat—a sizeable amount. Also, to *decompose* 102.0 g of Al_2O_3 into 54.0 g of aluminum metal and 48.0 g of oxygen gas, one must put 400.5 kcal of heat *into* the system—an amount equal in magnitude but opposite in sign from the heat of formation.

The heat of formation of any element in its standard state at 25°C and 1 atm of pressure (standard temperature and pressure) is always assigned 0 using this system. For example, the enthalpy of formation of carbon is zero for graphite, since graphite is the thermodynamically stable form of carbon found naturally at 25°C and 1 atm of pressure. However, the enthalpy of formation for carbon as diamond is 0.574 kcal/mol.

A chemical reaction can be considered to occur in two steps:

1. Decomposition of the starting materials into their constituent elements, followed by
2. Subsequent reaction of these elements to form the desired products.

The *net* heat change associated with the overall reaction can then be calculated from:

$$\Delta H(\text{reaction}) = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$$

(where $\sum$ = "the sum of")

This equation sums up the heats of formation of all of the products from a reaction and then subtracts from that value the heat required to dissociate all of the starting materials into their elements. The difference between these two values is the net heat change or heat of reaction. The heats of formation of a number of materials of interest to the high-energy chemist may be found in Table 2.10. All values given are for a reaction occurring at 25°C (298.15 K).

TABLE 2.10
Standard Heats of Formation at 25°C

Compound	Formula	ΔH_f (kcal/mol)[a]
Oxidizers		
Ammonium nitrate	NH_4NO_3	–87.4
Ammonium perchlorate	NH_4ClO_4	–70.58
Barium chlorate (hydrate)	$Ba(ClO_3)_2 \cdot H_2O$	–184.4
Barium chromate	$BaCrO_4$	–345.6
Barium nitrate	$Ba(NO_3)_2$	–237.1
Barium peroxide	BaO_2	–151.6
Iron oxide (red)	Fe_2O_3	–197.0
Iron oxide (black)	Fe_3O_4	–267.3
Lead chromate	$PbCrO_4$	–217.7[b]
Lead oxide (red lead)	Pb_3O_4	–171.7
Lead peroxide	PbO_2	–66.3
Potassium chlorate	$KClO_3$	–95.1
Potassium nitrate	KNO_3	–118.2
Potassium perchlorate	$KClO_4$	–103.4
Sodium nitrate	$NaNO_3$	–111.8
Strontium nitrate	$Sr(NO_3)_2$	–233.8
Fuels		
Elements		
Aluminum	Al	0
Boron	B	0
Iron	Fe	0
Magnesium	Mg	0
Phosphorus (red)	P	–4.2[c]
Phosphorus (white)	P_4	0
Silicon	Si	0
Titanium	Ti	0

(*Continued*)

TABLE 2.10 (*Continued*)
Standard Heats of Formation at 25°C

Compound	**Formula**	**ΔH_f (kcal/mol)**[a]
Organic Compounds[d]		
Lactose (hydrate)	$C_{12}H_{22}O_{11}\cdot H_2O$	−651
Shellac	$C_{16}H_{24}O_5$	−227
Hexachloroethane	C_2Cl_6	−54
Starch (polymer)	$(C_6H_{10}O_5)_n$	−227 (per unit)
Anthracene	$C_{14}H_{10}$	+32
Polyvinyl chloride (PVC)	$(-CH_2CHCl-)_n$	−23(per unit)[b]
Reaction Products		
Aluminum oxide	Al_2O_3	−400.5
Barium oxide	BaO	−133.4
Boron oxide	B_2O_3	−304.2
Carbon dioxide	CO_2	−94.1
Carbon monoxide	CO	−26.4
Chromium oxide	Cr_2O_3	−272.4
Lead oxide (litharge)	PbO	−51.5
Magnesium oxide	MgO	−143.8
Nitrogen	N_2	0
Phosphoric acid	H_3PO_4	−305.7
Potassium carbonate	K_2CO_3	−275.1
Potassium chloride	KCl	−104.4
Potassium oxide	K_2O	−86.4
Potassium sulfide	K_2S	−91.0
Silicon dioxide	SiO_2	−215.9
Sodium chloride	$NaCl$	−98.3
Sodium oxide	Na_2O	−99.0
Strontium oxide	SrO	−141.5
Titanium dioxide	TiO_2	−225
Water	H_2O	−68.3
Zinc chloride	$ZnCl_2$	−99.2

[a] Weast (1994).

[b] U.S Army Material Command (1967).

[c] Note that red phosphorus' enthalpy of formation is *not* zero, even though it is an elemental form. The allotrope white phosphorus is used as the "standard" form, which therefore has an enthalpy of formation of zero. Conversion from white to red phosphorus accounts for the negative enthalpy of formation.

[d] Shidlovskiy (1964).

Example 1

Consider the following reaction, balanced using the "oxidation numbers" or Pyro Valence method:

Reaction	**$KClO_4$**	**+**	**4 Mg**	**→**	**KCl**	**+**	**4 MgO**
Grams	138.6		97.2		74.6		161.2
Heat of formation (kcal/mol × # of moles)	−103.4		4 (0)		−104.4		4 (−143.8)

$$\begin{aligned}\Delta H(\text{reaction}) &= \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})\\ &= [-104.4 + 4(-143.8)] - [-103.4 + 4(0)]\\ &= -576.2 \text{ kcal/mol } KClO_4\\ &= -2.44 \text{ kcal/gram of stoichiometric mixture}\end{aligned}$$

(obtained by dividing -576.2 kcal by $138.6 + 97.2 = 235.8$ grams of starting material).

Example 2

Reaction	**4 KNO_3**	**+**	**5 C**	**→**	**2 K_2O**	**+**	**2 N_2**	**+**	**5 CO_2**
Grams	404.4		60		188.4		56		220
Heat of formation	4(−118.2)		5(0)		2(−86.4)		2(0)		5(−94.1)

$$\begin{aligned}\Delta H(\text{reaction}) &= \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})\\ &= [2(-86.4) + 0 + 5(-94.1)] - [4(-118.2) + 5(0)]\\ &= -643.3 - (-472.8)\\ &= -170.5 \text{ kcal/equation as written} (4 \text{ mol } KNO_3)\\ &= -42.6 \text{ kcal/mol } KNO_3\\ &= -0.37 \text{ kcal/gram of stoichiometric mixture} (-170.5 \text{ kcal}/464.4 \text{ g})\end{aligned}$$

RATES OF CHEMICAL REACTIONS

The preceding section discussed how the chemist can make a thermodynamic determination of the spontaneity of a chemical reaction. However, even if these calculations indicate that a reaction should be quite spontaneous (the value for ΔG is a large, negative number), there is no guarantee that the reaction will proceed rapidly when the reactants are mixed together at 25°C (298.15 K). For example, the reaction:

$$\text{Wood} + O_2 \rightarrow CO_2 + H_2O \tag{2.15}$$

has a large, negative value for ΔG at 25°C. However (of course), wood and oxygen are reasonably stable when mixed together at 25°C (a typical room temperature). The explanation of this thermodynamic mystery lies in another energy concept

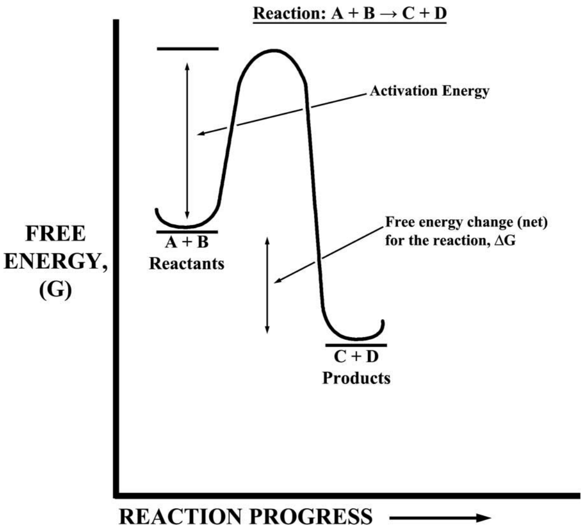


FIGURE 2.3 The free energy, *G*, of a chemical system, as reactants A and B, convert to products C and D. A and B must first acquire sufficient energy (activation energy) to be in a reactive state. As products C and D are formed, energy is released and the final energy level is reached. The *net* energy chance, Δ*G*, corresponds to the difference between the energies of the products and reactants. The *rate* at which a reaction proceeds is determined by the energy barrier that must be crossed—the activation energy.

known as the *energy of activation*. This term represents the amount of energy needed to take the starting materials from their reasonably stable form at 25°C and convert them to a reactive, higher-energy excited state. In this excited state, a reaction will occur to form the anticipated products, with the liberation of considerable energy—all the energy that was required to reach the excited state plus considerably more, which will be the *net* heat of reaction. Figure 2.3 illustrates the process.

The rate of a chemical reaction is determined by the magnitude of this required activation energy and rate is a temperature-dependent phenomenon. As the temperature of a system is raised, more energy is being added to the system and an exponentially greater number of molecules will possess the necessary energy of activation. The reaction rate will therefore increase accordingly in an exponential fashion as the temperature rises. This is illustrated in Figure 2.4.

Much of the pioneering work in this area of reaction rates was done by the Swedish chemist Svante Arrhenius, and the equation describing this rate–temperature relationship is known as the Arrhenius Equation:

$$k = Ae^{-E_a/RT} \tag{2.16}$$

where

k = the rate constant for a particular reaction at temperature T (this is a constant representing the speed of the reaction and is determined experimentally).
A = a temperature-independent constant for the particular reaction, termed the "pre-exponential factor."
e = Euler's number, the mathematical constant that is the source of natural logarithms and is approximately equal to 2.71828.
E_a = the activation energy for the reaction.
R = a universal constant known as the "ideal gas constant."
T = temperature, in Kelvin.

If the natural logarithm (ln) of both sides of Equation 2.16 is taken, one obtains:

$$\ln k = \ln A - E_a/RT \tag{2.17}$$

Therefore, if the rate constant, k, is measured at several temperatures and ln k versus $1/T$ is plotted, a straight line should be obtained, with slope of $-E_a/R$. Activation energies can be obtained for chemical reactions through such experiments. The Arrhenius Equation, describing the rate–temperature relationship, is of considerable significance in the processes leading to the ignition of energetic materials, and it will be referred to in subsequent chapters.

One other significant point that can be gleaned from the rate–temperature relationship is the fact that warm energetic materials (propellants and pyrotechnics in particular) will have a lower energy-of-activation hill to climb to undergo ignition than cold energetic materials, and therefore warm compositions will ignite easier and exhibit faster burn rates upon ignition. Numerous studies over the years have demonstrated

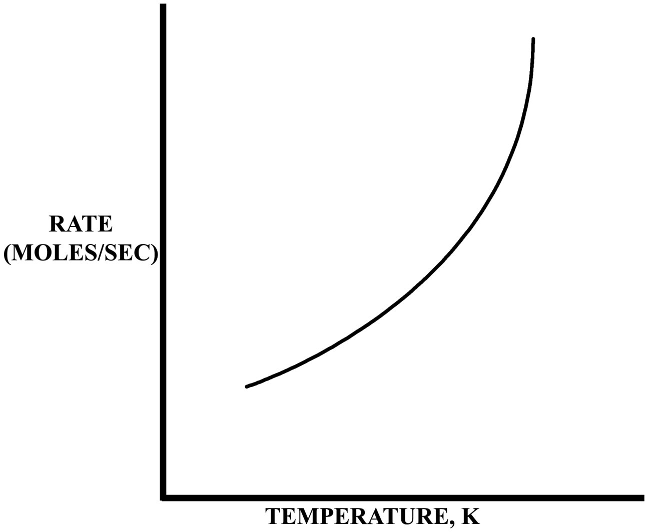


FIGURE 2.4 The effect of temperature on reaction rate. As the temperature of a chemical system is increased, the rate at which that system reacts to form products increases exponentially.

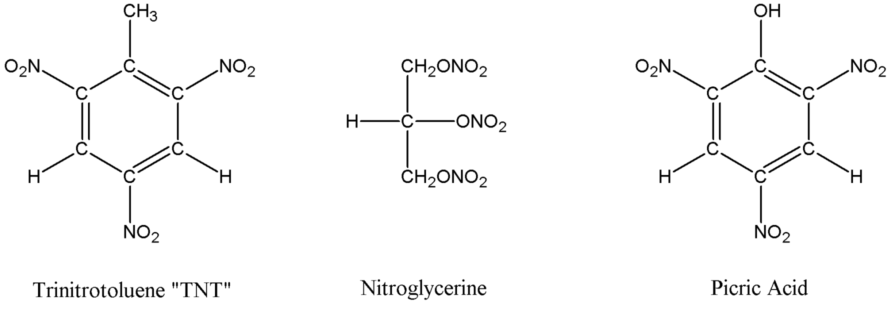
this phenomenon. The ambient temperature for materials from rocket propellant to highway flares will affect their performance, and this must be considered when comparing performance tests that have been run under different temperature conditions.

ENERGY-RICH BONDS

Certain covalent chemical bonds (such as N–O and Cl–O) are frequently encountered in the high-energy field. Bonds between two highly electronegative atoms tend to be less stable than ones between atoms of differing electronegativity. The intense competition for the electron density in a bond such as Cl–O is believed to be responsible for at least some of this instability. A modern chemical bonding theory known as the "molecular orbital theory" predicts inherent instability for some common high-energy species. The azide ion, N_3^-, and the fulminate ion, CNO^-, are examples of species whose unstable behavior is explainable using this approach (Pytlewski 1981).

In structures such as the nitrate ion, NO_3^-, and the perchlorate ion, ClO_4^-, a highly electronegative atom has a large, positive oxidation number (+5 for N in NO_3^-, +7 for Cl in ClO_4^-). Such large positive numbers indicate electron deficiency. It is therefore not surprising that structures with such bonding arrangements are particularly reactive as electron acceptors (oxidizers). It is for similar reasons that many of the nitrated carbon-containing (organic) compounds, such as nitroglycerine and TNT, are so unstable (Figure 2.5). The nitrogen atoms in these molecules want to accept electrons to relieve bonding stress, and the carbon atoms found in the same molecules are excellent electron donors.

In addition, if you assign partial charges to the atoms in many of these molecules, using Pauling's electronegativity concept, you wind up with many situations where adjacent carbon atoms bear partial positive charges. This has a destabilizing, bond-weakening effect on the molecular structure that is often reflected in causing the molecule to decompose at lower temperature or be more shock-sensitive. Nitroglycerine (Figure 2.5) is a good example—the three carbon atoms all possess partial positive charges due to the presence of a highly electronegative nitrate group on each carbon. The adjacent positively charged carbons will have a repelling effect



Trinitrotoluene "TNT" Nitroglycerine Picric Acid

FIGURE 2.5 Many "unstable" organic compounds are used as explosives. These molecules contain internal oxygen, usually bonded to nitrogen, an undergone intramolecular oxidation–reduction to form stable products—carbon dioxide, nitrogen, and water. The "mixing" of oxidizer and fuel is achieved at the molecular level, and *fast* rates of decomposition can be obtained.

on each other, thereby explaining—at least in part—the extremely sensitive nature of nitroglycerine to impact and shock.

Two very stable gaseous (high entropy) chemical species, N_2 and CO_2, are produced upon the decomposition reaction of most nitrated carbon-containing compounds, helping to insure a large, negative value for ΔG for the process (therefore making it spontaneous). These considerations make it mandatory that anyone working with nitrogen-rich carbon-containing compounds or with nitrate, perchlorate, and similar oxygen-rich negative ions must use extreme caution in the handling of these materials until their properties have been fully examined in the laboratory. Elevated temperatures should also be avoided when working with potentially unstable materials, because of the rate–temperature relationship that is exponential in nature. A non-existent or sluggish process can become an explosion when the temperature of the system is sharply increased.

STATES OF MATTER

With few exceptions, the high-energy chemist deals with materials that are in the solid state at normal room temperature. This provides for dimensional stability when the materials are loaded into end items, and this is very helpful in ensuring relatively long storage lifetimes for energetic devices. Solids mix very slowly with one another and hence they tend to be more sluggish in their reactivity than mixtures of gases, where a homogeneous state can be reached very quickly. Liquids also reach a homogeneous state quickly, provided the liquids are "miscible" and can mix to become homogenous (oil and water being an example of *immiscible* liquids). Rapid reactivity with solid systems is usually associated with the formation, at higher temperatures, of liquid or gas states. Species in these states can diffuse into one another more rapidly, leading to accelerated reactivity.

In pyrotechnics, the solid-to-liquid transition appears to be of considerable importance in initiating a self-propagating reaction in many systems. The oxidizing agent is frequently the key component in such mixtures, and a ranking of common oxidizers by increasing melting point bears a striking resemblance to the reactivity sequence for these materials (Table 2.11). The other significant factor here is that

TABLE 2.11
Melting Points of Some Common Oxidizers

Oxidizer	Formula	Melting Point, °C[a]
Potassium nitrate	KNO_3	334
Potassium chlorate	$KClO_4$	356
Barium nitrate	$Ba(NO_3)_2$	592
Potassium perchlorate	$KClO_4$	610
Strontium nitrate	$Sr(NO_3)_2$	570
Lead chromate	$PbCrO_4$	844
Iron oxide (red)	Fe_2O_3	1,565

[a] Weast (1994).

many of the common oxidizers used in pyrotechnics begin to undergo decomposition with the evolution of oxygen gas as they approach their melting point, and thereby facilitate the ignition process—this will be discussed in more detail in Chapter 6.

A change of state also involves an energy change. Going from solid to liquid or liquid to gas, normally requires a net input of energy into a system. Both the liquid state and the solid state are held together by attractive forces between the atoms, molecules, or ions making up the material. These attractive forces must be broken or weakened to go from solid to liquid and must be completely overcome for the liquid state to convert to vapor. The reverse of these directions (i.e., water vapor condensing to liquid water) is associated with an exothermic process, as the attractive forces interact and release energy.

While a phase change is underway, a system will remain at constant temperature (e.g., the melting of ice at 0°C and 1 atm pressure or the boiling of water at 100°C and 1 atm pressure). This is a very significant factor in the ignition process for an energetic material, since no temperature rise will occur while a phase change is underway. Hence, water-wet pyrotechnic composition (or wet wood in your fireplace) *cannot* get warmer than 100°C (212°F) until all of the water present has been driven off. If the ignition temperature of the material exceeds this temperature, ignition will not occur until the water has been removed and the temperature of the material rises to its ignition point. For the wood in your fireplace, the ignition temperature is near the infamous value of Fahrenheit 451, the ignition temperature of cellulose/paper—made famous by Ray Bradbury in the book of that title.

GASES

On continued heating, a pure material passes from the solid to liquid to vapor state, with continued absorption of heat. The volume occupied by the vapor is much greater than that of the solid and liquid phases. One mole (18 g) of water occupies approximately 18 mL (0.018 L) as a solid or liquid. One mole of water vapor, however, at 100°C (373.15 K) occupies approximately 30.6 L at normal atmospheric pressure. The volume occupied by a gas can be estimated using the *ideal gas equation* (Equation 2.18).

$$V = nRT/P \tag{2.18}$$

where

V = volume occupied by the gas, in liters
n = # of moles of gas
R = a constant, 0.0821 liter-atm/deg-mole
T = temperature, in K
P = pressure, in atmospheres

This equation is obeyed quite well by the inert gases (helium, neon, etc.) and by small diatomic molecules such as H_2 and N_2. Molecules possessing polar covalent bonds tend to have strong intermolecular attractions and usually deviate from "ideal" behavior—producing lower than expected pressures for a specified temperature.

Equation 2.18 remains a fairly good estimate of volume and pressure even for these polar molecules, however. Using the ideal gas equation, one can readily estimate the pressure produced during ignition of a confined high-energy composition.

For example, assume that 200 mg (0.200 g) of black powder is confined in a volume of 0.1 mL. Black powder burns to produce approximately 50% gaseous products and 50% solids. Approximately 1.2 mol of permanent gas are produced per 100 g of powder burned (the gases are mainly N_2, CO_2, and CO) (Military Pyrotechnic Series Part Three: "Properties of Materials Used in Pyrotechnic Compositions" 1963). Therefore, 0.200 g should produce 0.0024 mol of gas, at a temperature near 2,000 K. The expected pressure is:

$$P = \frac{(0.0024\,\text{mol})(0.0821\,\text{L-atm/deg-mole})(2000\,^\circ)}{(0.0001\,\text{L})} = 3{,}941\,\text{atm!}$$

Needless to say, the casing will rupture and an explosion will be observed. Burning a similar quantity of a good-quality black powder in the open, where little pressure accumulation occurs, will produce a slower, less violent (but still quite vigorous) reaction and no explosive effect. This significant dependence of burning behavior on degree of confinement is an important characteristic of pyrotechnic mixtures and distinguishes them from true high explosives, where confinement plays a relatively minor role in determining detonation velocity.

LIQUIDS

Gas molecules are widely separated, traveling at high speeds while colliding with other gas molecules and with the walls of their container. Pressure is produced by these collisions with the walls and depends upon the number of gas molecules present as well as their kinetic energy. Their speed, and therefore their kinetic energy, increases with increasing temperature.

As the temperature of a gas system is lowered, the speed of the molecules decreases. When these lower-speed molecules collide with one another, attractive forces between the molecules become more significant, and a temperature will be reached where *condensation* occurs—the vapor state converts to liquid. Dipole–dipole attractive forces are most important in causing condensation, and the molecules with substantial partial charges, resulting from polar covalent bonds, typically have high condensation temperatures. (Condensation temperature will be the same as the boiling point of a liquid, approached from the opposite direction.)

The liquid state has a minimum of order, and the molecules have considerable freedom of motion. A drop of food coloring placed in water demonstrates the rapid diffusion that can occur in the liquid state. The solid state will exhibit no detectable diffusion. If this experiment is tried with a material such as iron, the liquid food coloring will merely form a drop on the surface of the metal.

At the liquid surface, molecules can acquire high vibrational and translational energy from their neighbors, and one will occasionally break lose to enter the vapor state. This phenomenon of vapor above a liquid surface is termed vapor pressure and will lead to gradual evaporation of a liquid unless the container is covered. In this case, an *equilibrium* is established between the molecules entering the vapor state per minute and the molecules re-condensing on the liquid surface. The pressure of gas molecules above a liquid in a confined system is a constant for a given material at a given temperature and is known as the *equilibrium vapor pressure.* It increases exponentially with increasing temperature. When the vapor pressure of a liquid is equal to the external pressure acting on the liquid surface, boiling occurs. For solids and liquids to undergo sustained burning, the presence of a portion of the fuel in the vapor state is required.

THE SOLID STATE

The solid state is characterized by definite structure and volume. The observed structure will be the one that maximizes favorable interactions between the atoms, ions, or molecules making up the solid state. The preferred packing arrangement begins at the atomic or molecular level and is regularly repeated throughout the solid, producing a highly symmetrical, three-dimensional form called a *crystal.* The network produced is termed the *crystalline lattice.*

Solids lacking an ordered, crystalline arrangement are termed *amorphous* materials and resemble rigid liquids in structure and properties. Glass (SiO_2) is the classic example of an amorphous solid. Such materials typically soften on heating, rather than showing a sharp melting point.

In the crystalline solid state, there is little vibrational or transitional freedom and hence diffusion into a crystalline lattice is slow and difficult. As the temperature of a solid is raised by the input of heat, vibrational and transitional motion increases. At a particular temperature—termed the melting point—this motion overcomes the attractive forces holding the lattice together and the liquid state is produced. The liquid state, on cooling, returns to the solid state as crystallization occurs and heat is released by the formation of strong attractive forces. The melting points of some common solid pyrotechnic oxidizers (or the "freezing point" from the opposite direction if the oxidizers were in the liquid state) are listed in Table 2.11.

The types of solids, categorized according to the particles that make up the crystalline lattice, are listed in Table 2.12.

TABLE 2.12
Types of Crystalline Solids

Type of Solid	Units Comprising Crystal Lattice	Attractive Force	Examples
Ionic	Positive and negative ions	Electrostatic attraction	KNO_3, NaCl
Molecular	Neutral molecules	Dipole-dipole attractions, plus weaker, non-polar forces	CO_2 ("dry ice"), sugar
Covalent	Atoms	Covalent bonds	Diamond (carbon)
Metallic	Metal atoms	Dispersed electrons attracted to numerous metal atom nuclei	Fe, Al, Mg

The type of crystalline lattice formed by a solid material depends on the size and shape of the lattice units, as well as on the nature of the attractive forces. Six basic crystalline systems are possible (Military Pyrotechnic Series Part One, “Theory and Application” 1967):

1. Cubic: three axes of equal length, intersecting at all right angles
2. Tetragonal: three axes intersecting at right angles; only two axes are equal in length
3. Hexagonal: three axes of equal length in a single plane intersecting at 60° angles; a fourth axis of different length is perpendicular to the plane of the other three
4. Rhombic: three axes of unequal length, intersecting at right angles
5. Monoclinic: three axes of unequal length, two of which intersect at right angles
6. Triclinic: three axes of unequal length, none of which intersect at right angles

To this point, our model of the solid state has suggested a placement of every lattice object at the proper site in order to create a “perfect” three-dimensional crystal. Research into the actual structure of solids has shown that crystals are far from perfect, containing a variety of types of defects. Even the purest crystals, modern chemistry can create, contain large numbers of impurities and “misplaced” ions, molecules, or atoms in the lattice. These inherent defects can play an important role in the reactivity of solids by providing a mechanism for the transport of electrons and heat through the lattice. They also can greatly enhance the ability of another substance to diffuse into the lattice, thereby again affecting reactivity (McLain 1980).

A commonly observed phenomenon associated with the presence of impurities in a crystalline lattice is a depression in the melting point of the solid, with the solid → liquid transition occurring over a broad range rather than displaying the sharp melting point at higher temperature that is observed with a purer material. Melting behavior thereby provides a convenient means of checking the purity of solids, a property that can be quite useful to quality assurance laboratories examining incoming shipments of chemicals for use in manufacturing energetic mixtures.

An important factor in the ignition and propagation of burning of pyrotechnic compositions is the conduction of heat along a column of the mixture. Hot gases serve as excellent heat carriers and can be a significant burn rate factor in porous compositions, but frequently the heat must be conducted by the solid state, ahead of the reaction zone. Heat can be transferred by molecular motion as well as by free, mobile electrons (Military Pyrotechnic Series Part One, “Theory and Application” 1967). The thermal conductivity values of some common materials are given in Table 2.13. Examining this table, one can readily see how the presence of a small quantity of metal powder in a pyrotechnic composition can greatly increase the thermal conductivity of the mixture and thereby increase the burning rate by pre-heating the column of burning material ahead of the actual reaction zone.

TABLE 2.13
Thermal Conductivity Values for Solids[a]

Material	Thermal Conductivity (× 10^3), cal/s cm °C
Copper	910
Aluminum	500
Iron	150
Glass	2.3
Oak wood	0.4
Paper	0.3
Charcoal	0.2

[a] Tuye (1976).

OTHER PHASES OF MATTER

The three most common phases of matter seen naturally on Earth under normal conditions are solids, liquids, and gases. However, other states of matter that do not fit neatly into the definitions for the three common phases are also known to exist.

"Plasma" is a fourth common phase of matter seen almost every day: "neon" signs, lightening, and fluorescent light bulbs are all examples of the plasma state. Plasma is a gaseous state where the neutral gaseous atoms are forcibly ionized (the electrons are pulled from their orbitals with sufficient intense energy) with the newly free electrons now "mixed in" with the gaseous ions (and therefore also electrically conductive). The high energy of the plasma also leads the constant collision of particles in the plasma and the emission of light, which is why plasmas glow. This state of matter occurs when a substance is heated to sufficiently high temperatures, exposed to sufficiently high voltages, or encounters some other source of high-energy release (such as a shock wave or nuclear fission/fusion) that is sufficient to pull electrons from their shells (Rose and Rose 1961). The sun and stars are another example of plasma material. Most flames generated from pyrotechnic reactions probably contain some amount of plasma, although to varying amounts (Von Engel and Cozens 1964).

Other much less common phases of matter include very low temperature Bose–Einstein Condensates (which only exist near absolute zero, 0 K or –273.15°C) and very high energy quark-gluon plasmas (which exist at trillions of Kelvin in temperature) to name two. These and other highly uncommon and theoretical states, while fascinating to explore, do not have much bearing on day-to-day pyrotechnics.

ACIDS AND BASES

There are several concepts and theories for acid–base reactions but the one most useful in pyrotechnics is Brønsted–Lowry acid–base theory, named after the scientists who independently developed the model. In this concept, an *acid* is commonly described as a molecule or ion that can serve as a hydrogen ion (H^+) donor. The hydrogen ion is identical to the proton—it contains one proton in the nucleus and has no electrons surrounding the nucleus. H^+ is a light, mobile, reactive species. A *base* is a species that functions as a hydrogen ion acceptor, such as a hydroxide ion, OH^-. The transfer of a hydrogen ion (proton) from a good donor to a good acceptor is called an acid–base reaction. Materials that are neither acidic nor basic in nature are said to be *neutral*, while those that can act as both an acid and a base (such as water) are called *amphoteric*.

Hydrogen chloride (HCl) is a gas that readily dissolves in water. In water, HCl is called hydrochloric acid, and the HCl molecule serves as a good proton donor readily undergoing the reaction

$$\mathrm{HCl} \rightarrow \mathrm{H}^+ + \mathrm{Cl}^-$$

to produce a hydrogen ion and a chloride ion in solution. The concentration of hydrogen ions in water can be measured by a variety of methods and provides a measure of the acidity of an aqueous system. The most common measure of acidity is pH, a number representing the negative common logarithm of the hydrogen ion concentration:

$$\mathrm{pH} = -\log\left[\mathrm{H}^+\right] \tag{2.19}$$

If a solution also contains hydroxide ion (OH^-), a good proton acceptor, the reaction

$$\mathrm{H}^+ + \mathrm{OH}^- = \mathrm{H_2O}$$

occurs, forming water—a neutral species. The overall reaction is represented by an equation such as

$$\mathrm{HCl} + \mathrm{NaOH} = \mathrm{H_2O} + \mathrm{NaCl}$$

Acids usually contain a bond between hydrogen and an electronegative element such as F, O, or Cl. The electronegative element pulls electron density away from the hydrogen atom, giving it partial positive character and making it willing to leave as H^+. The presence of additional F, O, and Cl atoms in the molecule further enhances the acidity of the species. Examples of strong acids include sulfuric acid (H_2SO_4), hydrochloric acid (HCl), perchloric acid ($HClO_4$), and nitric acid (HNO_3).

Most of the common bases are ionic compounds consisting of a positive metal ion and the negatively charged hydroxide ion, OH^-. Examples include sodium hydroxide (NaOH), potassium hydroxide (KOH), and calcium hydroxide, $Ca(OH)_2$. Ammonia (NH_3) is a weak base, capable of reacting with H^+ to form the ammonium ion, NH_4^+.

Acids catalyze a variety of chemical reactions, even when present in small quantity. The presence of trace amounts of acidic materials in many high-energy compounds and mixtures can lead to instability. The chlorate ion, ClO_3^-, is notoriously unstable in the presence of strong acids. Chlorate-containing pyrotechnic mixtures will usually ignite if a drop of concentrated sulfuric acid is added.

Many metals are also vulnerable to acids, undergoing an oxidation–reduction reaction that produces the metal ion and hydrogen gas (which is flammable). The balanced equation for the reaction between HCl and magnesium is

$$\mathrm{Mg} + 2\mathrm{HCl} \rightarrow \mathrm{Mg}^{2+} + \mathrm{H_2} + 2\mathrm{Cl}^- + \text{heat}$$

Consequently, most metal-containing compositions must be free of acidic impurities, or extensive decomposition (and possibly ignition) may occur.

As protection against acidic impurities, high-energy mixtures will frequently contain a small percentage of a neutralizer. Sodium bicarbonate ($NaHCO_3$) and magnesium carbonate ($MgCO_3$) are two frequently used materials. The carbonate ion, CO_3^{2-}, reacts with H^+

$$2H^+ + CO_3^{2-} \rightarrow H_2O + CO_2$$

to form two neutral species—water and carbon dioxide.

Boric acid (H_3BO_3)—a solid material that is a weak H^+ donor—is sometimes used as a neutralizer for base-sensitive compositions. Mixtures containing aluminum metal and a nitrate salt are notably sensitive to excess hydroxide ion, and a small percentage of boric acid can be quite effective in stabilizing such compositions.

LIGHT EMISSION

The pyrotechnic phenomena of heat, smoke, noise, and motion are reasonably easy to comprehend. Heat results from the rapid release of energy associated with the formation of stable chemical bonds during a chemical reaction. Smoke is produced by the dispersion of many small particles during a chemical reaction. Noise is produced by the rapid generation of gas at high temperature, creating compression waves that travel through air (sometimes at or even greater than, the "speed of sound," 340 m/s). Motion can be produced if you direct the hot gaseous products of a pyrotechnic reaction through an exit, or nozzle. The thrust that is produced can move an object of considerable mass, if sufficient propellant is used.

The theory of color and light production, however, involves the energy levels available for electrons in atoms and molecules, according to the understanding of modern chemical theory. In an atom or molecule, there are a number of "orbitals" or energy levels that an electron may occupy. Each of these levels corresponds to a discrete energy value, and *only* these energies are possible. The energy is said to be *quantized* or restricted to certain values that depend on the nature of the particular atom or molecule. We can represent these allowed electronic energies by a diagram such as Figure 2.6 for sodium (which has 11 electrons).

Logic suggests that an electron will occupy the lowest energy level available, and electrons will successively fill these levels as they are added to an atom or molecule. "Quantum mechanics" restricts all orbitals to a maximum of two electrons (these two have opposite "spins" and do not strongly repel one another), and hence a filling process occurs where no two electrons are identical, that is, occupying the same orbital and having the same spin. The filling pattern for the sodium atom (sodium is atomic number 11—therefore there will be 11 electrons in the neutral atom) is shown in Figure 2.6.

When energy is put into a sodium atom, in the form of heat or light, one means of accepting this energy is for an electron to be "promoted" to a higher energy level. The electron in this "excited state" is unstable and it will tend to quickly return to the "ground state" with the release of an amount of energy exactly equal to the energy

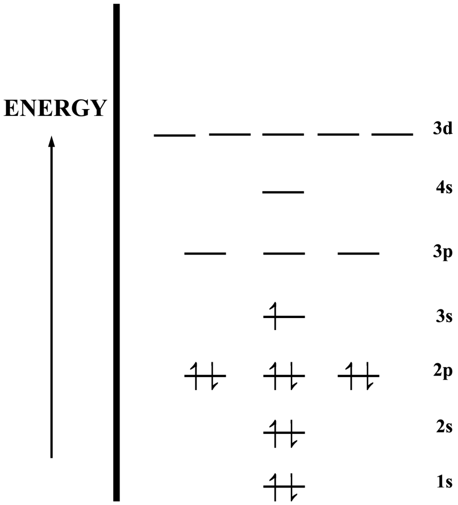


FIGURE 2.6 The energy levels of the sodium atom. The sodium atom contains 11 electrons. These electrons will successively fill the lowest available energy levels in the atom, with a maximum population of two electrons in any given "orbital." The experimentally determined energy level sequence is shown in this figure, with the 11th (and highest-energy) electron places in the 3s level. The lowest vacant level is a 3p orbital. To raise an electron from the 3s to the 3p level requires 3.38×10^{-19}J of energy. This energy corresponds to light of 589 nm wavelength—the yellow portion of the visible spectrum. Sodium atoms heated to high temperature will *emit* this yellow light as electrons are thermally excited to the 3p level, and then return to the 3s level and give off the excess energy as yellow light.

difference between its ground and excited states. For the sodium atom, the difference between the highest occupied and lowest unoccupied levels is 3.38×10^{-19} J/atom. This energy can be lost as an emission of heat to the surroundings upon return to the ground state or it can be released as a unit, or "photon", of light.

Light, or electromagnetic radiation, has both wave and particle unit character associated with its behavior. Wavelengths range from very short (10^{-12}m) for the "gamma rays" that accompany radioactive decay to quite long (10 m) for radio waves.

All light travels at the same speed in a vacuum, with an approximate value of 3×10^{8} m/s—the "speed of light." This value can also be used for the speed of light in air for convenience purposes.[5]

The wavelength of light can now be related to the frequency, or number of waves passing a given point per second, using the speed of light value:

$$\text{frequency}(\nu) = \frac{\text{speed}(c)}{\text{wavelength}(\lambda)}$$

---

[5] The speed of light slows in a medium other than a total vacuum due to photons of light interacting with atoms and particles that the photons encounter. However, the speed of light in air is only a tiny fraction slower than that in a vacuum, hence using the same value for simplicity.

$$\left(\text{waves/second}\right)=\frac{\left(\text{meters/second}\right)}{\left(\text{meters/wave}\right)}$$

The entire range of wavelengths comprising "light" is known as the *electromagnetic spectrum* as show in Figure 2.7.

We can readily tell that light is a form of energy by staying out in the sun for too long at a time. Elegant experiments by Einstein and others clearly showed that the energy associated with light was directly proportional to the frequency of the radiation:

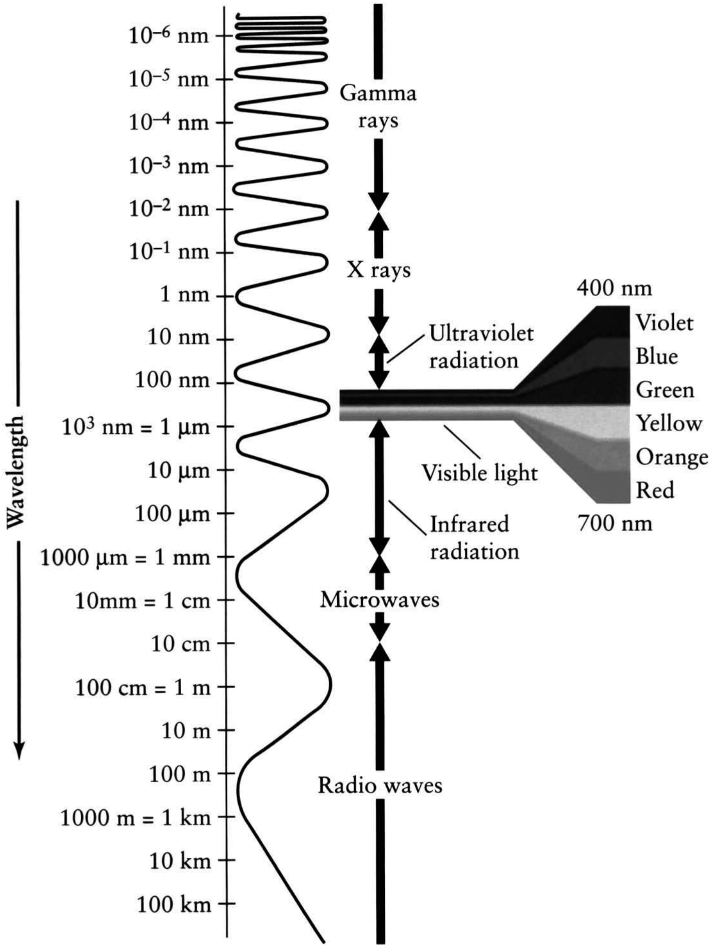


FIGURE 2.7 The electromagnetic spectrum. The various regions of the electromagnetic spectrum correspond to a wide range of wavelengths, frequencies, and energies. As wavelength decreases, energy increases, and vice-versa. The radiofrequency range is at the long-wavelength, low-energy end, with gamma rays at the short-wavelength, high-frequency, high-energy end. The "visible" region—that portion of the spectrum perceived as color by the human visual system—falls in the narrow region from 380 to 780 nm (1 nm = 10^{-9}m).

$$E = h(\nu) = h(c/\lambda) \tag{2.20}$$

Where

E = the energy per light particle (photon)
h = a constant, Planck's constant, 6.63×10^{-34} J s
ν = frequency of light (in waves—"cycles"—per second)
c = speed of light (~3×10^{8} m/s)
λ = wavelength of light (in meters)

This equation permits one to equate a wavelength of light with the energy associated with a photon of that particular radiation. For the sodium atom, the wavelength of light corresponding to the energy difference of 3.38×10^{-19} J between the highest occupied and the lowest unoccupied electronic energy levels should be:

$$E = h(c/\lambda)$$

rearranging:

$$\begin{aligned} \lambda &= h(c/E) \\ &= \frac{(6.63 \times 10^{-34}\ \text{J s})(3 \times 108\ \text{m/s})}{(3.38 \times 10^{-19}\ \text{J})} \\ &= 5.89 \times 10^{-7}\ \text{m} \\ &= 589\ \text{nm}\left(\text{where } 1\ \text{nm} = 10^{-9}\ \text{m}\right) \end{aligned}$$

Light of wavelength 589 nm falls into (what your eyes and brain perceive as) the yellow–orange portion of the *visible* region of the electromagnetic spectrum. The characteristic yellow–orange glow of sodium vapor lamps used to illuminate many highways results from this particular emission.

To produce this type of atomic emission in a pyrotechnic system, one must produce sufficient heat to generate atomic vapor in the flame and then excite the atoms from the ground to various possible excited electronic states. Emission intensity will increase as the flame temperature increases, as more and more atoms are vaporized and excited. Return of the electrons to their original orbitals, and therefore atoms to their ground state, produces the light emission. A pattern of wavelengths, known as an *atomic spectrum*, is produced by each element. This pattern—a series of lines—corresponds to the various electronic transitions possible for the particular atom. The pattern is characteristic for each element and can be used for qualitative identification purposes.

MOLECULAR EMISSION

A similar phenomenon is observed when molecules are vaporized and thermally excited. Electrons can be promoted from an occupied ground electronic state (orbital) to a vacant excited state; when as electron returns to the ground state, a photon of light may be emitted.

Molecular spectra are usually more complex than atomic spectra. The energy levels are more complex and vibrational and rotational sublevels superimpose their patterns on the electronic spectrum. *Bands* are generally observed rather than the sharp lines seen in atomic spectra. Emission intensity again increases as the flame temperature is raised. However, one must be concerned about reaching too high a temperature and decomposing the molecular emitter; the light-emission pattern will change if this occurs. This is a particular problem in achieving an intense blue flame. One of the best blue-light emitters—copper chloride (CuCl)—becomes unstable at high-flame temperatures (see Chapter 10).

"BLACK BODY" RADIATION/EMISSION

The presence of solid particles in a pyrotechnic flame can lead to a substantial loss of color purity due to a complex process known as "black-body radiation." Solid particles, as they are heated to high temperature, begin to radiate in the infrared region and give a sensation of warmth if you bring such a heated object near your skin. As the temperature of the heated object continues to increase, the emission begins to shift into the visible region, radiating a continuous spectrum of light, much of it in the visible region, with the intensity exponentially increasing with temperature. If you are attempting to produce white light (which is a combination of *all* wavelengths in the visible region), this incandescent phenomenon is desirable. Conversely, if the intention is to produce a particular color, excessive black-body radiation can wash out the desired color.

Magnesium metal is found in many "white light" formulas. In an oxidizing flame, the metal is converted to the high-melting magnesium oxide, MgO, an excellent white-light emitter by incandescence. Also, the high heat output of magnesium-containing compositions aids in achieving high-flame temperatures. Aluminum metal is also commonly used for light production; other metals, including titanium and zirconium, are also good white-light sources.

Note: Many of the "white-light" compositions used by the military contain sodium nitrate as the oxidizer and magnesium as a fuel, with a carbon–hydrogen binder to hold the materials in a homogeneous blend. The combination of intense light emission from the vapor–phase sodium atoms and the solid magnesium oxide incandescent particles produce a bright white-light effect when the composition burns at a temperature above 3,000°C (Dillehay 2004).

The development of color and light-producing compositions will be considered in more detail in Chapter 10.

"GREEN" CHEMISTRY AND PYROTECHNICS: AN INTRODUCTION

The effects of modern chemicals on our environment and on the health of human beings and other animals have been an increasingly important topic as scientists learn more about their properties. Research in environmental chemistry and science has been critical to understanding how industrial, commercial, and day-to-day household use of substances can have a dramatic influence—sometimes good, sometimes bad—on the world around us in occasionally very complicated ways. As undesirable effects of chemicals—such as toxicity to humans or damage to plants—are discovered, governments and other institutions have begun to regulate, reduce, or even eliminate the use of suspect chemicals to avoid ill effects. The world of pyrotechnics (as well as propellants and explosives) is no different and is at the forefront of modern pyrotechnics research (Cumming 2017).

The colloquial term "green chemistry" has been used to describe using less toxic/more environmentally friendly substitute chemicals in place of those with more harmful effects. Concomitantly, we will use the term "green pyrotechnics" to refer to the same function in energetic materials: using less harmful chemicals in place of more harmful ones in pyrotechnic compositions and, hopefully, achieving the same effect. For example, in "green pyrotechnics," bismuth trioxide (Bi_2O_3) can be used in place of lead tetroxide (Pb_3O_4) as an oxidizer in "dragon egg" pyrotechnic formulations to achieve the requisite "crack" sound without the use of lead or generation of lead vapor (being more toxic to animals than bismuth). Another example is using other oxidizers in place of perchlorate $\left(ClO_4^-\right)$ ions, which has been shown to effect proper thyroid gland action by inhibiting the uptake of iodine, affecting the endocrine system (Srinivasan and Viraraghavan 2009). Since perchlorate is particularly soluble in water, removing perchlorate from the environment is a difficult task, and therefore replacing it in pyrotechnic compositions with another, less toxic chemical oxidizer has become a common goal in the world of pyrotechnics.

The challenge for pyrotechnicians is to find substitutes for undesirable chemicals without loss of performance in the overall composition: similar burn rate, similar color output or intensity, similar storage requirements, similar sensitivity to ignition, similar overall physical properties, and similar (or even reduced) costs. While this area has been studied on the peripheries of pyrotechnics research for decades, the recent push for research in "green" pyrotechnics has started to yield many interesting results for substitutions in pyrotechnic formulations. Enough work has been published that Tore Brinck of the Swedish Royal Institute of Technology has recently edited a *Green Energetic Materials* book that provides both an introduction to "green pyrotechnics" as well as several chapters on the latest research in the area (Brinck 2014).

We will consider recent research in "green pyrotechnics" in the discussion of various concepts as they are relevant in subsequent chapters but is by no means exhaustive in the ongoing study in this area.

CHEMICAL PRINCIPLES: A FINAL NOTE

While heavy textbooks and entire academic years (and sometimes even whole careers) are dedicated to the study of the basic chemical principles described here, this brief overview provides a foundation for the pyrotechnic principles that will be discussed in the remaining chapters.

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3 Components of Energetic Compositions

BLACK POWDER COMPONENTS: potassium nitrate (white), charcoal (black), and sulfur (yellow) are blended for hours to produce a homogeneous blend that has the reactivity associated with high-quality black powder. Purity of the starting chemicals, the “right” ratio of the three components by weight, and a proper mixing process are all necessary for a successful manufacturing process.

It may have begun with an early chef, somewhere in Asia, working over his cooking fire. He noticed that the saltpeter (potassium nitrate) he was using to season the evening meal caused the fire to glow more intensely when it hit the flames. Curiosity aroused, he then mixed the saltpeter with his charcoal and produced a burning mixture, but it was difficult to light. By adding a bit of brimstone (sulfur) to the mixture, the ignitibility improved. After a lot of trial and error, the end result was a material that changed the world: black powder. This unique blend of potassium nitrate, charcoal, and sulfur illustrates so well how the selection of chemicals is critical to the development of a successful pyrotechnic composition.

INTRODUCTION

Compounds containing both a readily oxidized and a readily reduced component within one molecule (such as trinitrotoluene, or TNT, with formula $C_7H_5N_3O_6$) or within one ionic compound such as ammonium nitrate (NH_4NO_3) are uncommon since such species tend to have explosive properties. A molecule or ionic compound containing an internal oxidizer–reducer pair is inherently the most intimately mixed, high-energy material that can be prepared. The mixing is achieved at the *molecular* (or *ionic*) level, and no migration or diffusion is required to bring the electron donor and electron acceptor together. The electron transfer reaction is *expected* to be rapid (even violent) in such species, upon application of the necessary activation energy to a small portion of the composition.

A variety of compounds possessing this *intramolecular* reaction capability are shown in Table 3.1. The output from the exothermic decomposition of these compounds is typically heat, gas, and shock. Many of these materials *detonate*—a property quite uncommon with physical mixtures, where the degree of homogeneity is considerably less and reaction times tend to be significantly longer. Many explosive molecules have the general molecular formula $C_aH_bN_cO_d$. The number and placement of the electronegative nitrogen and oxygen atoms serve to draw electron density away from carbon atoms. If the resulting partially positive carbon atoms are adjacent to one another, the carbon–carbon bond is weakened and the molecule may become shock-sensitive and the result is a molecular explosive. The nitroglycerine molecule illustrates this concept well. The molecule $C_3H_5N_3O_9$ has a chain of three adjacent carbon atoms. Each carbon atom is bonded to an oxygen atom, which in turn is bonded to a nitrogen atom with two more oxygen atoms attached. The highly electronegative oxygen and nitrogen atoms (see Chapter 2) cause a partially positive charge to exist on each carbon atom, and the resulting repulsive forces cause the carbons to repel each other, weakening the bonds.[1]

TABLE 3.1
Some Compounds Containing Intramolecular Oxidation–Reduction Capability

Compound	Formula
Ammonium nitrate	NH_4NO_3
Ammonium perchlorate	NH_4ClO_4
Lead azide	$Pb(N_3)_2$
Trinitrotoluene (TNT)	$C_7H_5N_3O_6$
Nitroglycerine (NG)	$C_3H_5N_3O_9$
Mercury fulminate	$Hg(ONC)_2$

Note: These compounds readily undergo explosive decomposition when sufficient ignition stimulus is applied. A shock stimulus is frequently needed to activate the non-ionic organic molecules (such as TNT); these compounds will often merely burn if just a flame is applied.

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[1] This is a condition that is akin to having "3 cats in a bag." If you don't know what this means, select at random three mature tomcats and cautiously place them together in a burlap sack and observe the resulting situation. "Unstable" describes both the cat situation, as well as the state of the nitroglycerine molecule.

The high-energy chemist can greatly expand his repertoire of materials by preparing *mixtures*, combining an oxidizing material with a fuel to produce the exact heat output and burning rate needed for a particular application. Although detonations are far less likely to occur with these physical mixtures (though not impossible by any means), propulsion, bright light, colors, thermal effects, hot particles, and smoke can be produced using such compositions, expanding the effects that can be achieved with high-energy materials in propellant and pyrotechnic articles. For these effects to occur, it is critical that the mixture *burn* rather than *explode* (in most cases, with a few exceptions). Burning behavior is dependent upon a number of factors, and the pyrotechnician must carefully control these variables to obtain the desired performance.

Pyrotechnic mixtures "burn," but it must be remembered that these compositions—unlike most materials that undergo combustion—*supply their own oxygen* for combustion, through the thermal decomposition of an oxygen-rich material such as potassium chlorate:

$$2KClO_3 + \text{heat} \rightarrow 2KCl + 3O_2 \tag{3.1}$$

Thus, *a pyrotechnic fire cannot be suffocated*: no atmospheric oxygen is needed for these mixtures to vigorously burn. In fact, confinement can *accelerate* the burning of an energetic composition by producing an increase in pressure, holding the heat at the reactive surface and possibly leading to an explosion. Adequate venting is quite important in keeping a pyrotechnic fire from developing into a serious explosion. The only way to get a pyrotechnic fire under control is to reduce the temperature of the burning material to a value less than the ignition temperature of the composition, and a cooling material (water, perhaps, and a lot of it) must be applied very quickly to even have a *chance* at stopping the reaction.

The selection of components for a particular energetic composition should be made using chemical logic, taking into consideration the desired heat output, burn rate, light intensity, color value, efficiency, ignitibility, and physical state of the reaction products (i.e., solid vs. gas). Factors such as availability, toxicity, stability, and environmental compatibility—and, of course, cost—must also be taken into consideration. The final blend of components must produce the desired output, be safe to prepare and use, have a long storage lifetime, use readily available components that are moderate in cost, and meet toxicological and environmental requirements.

These requirements quickly reduce the field of available materials for most energetic applications. There are few, if any, "exotic" chemicals that are widely used in producing energetic materials. For example, we will discuss iron oxide at several locations in the following chapters, but other oxidizers, such as ruthenium tetroxide (RuO_4), will not be discussed for reasons of cost, stability, and toxicity.

A variety of ingredients, each serving one or more purposes, can be used to create an effective pyrotechnic composition. These materials are discussed in varying detail in several excellent sources (Shidlovskiy 1964; Shimizu, Fireworks—*The Art, Science and Technique* 1981; Military Pyrotechnic Series Part Three: "Properties of Materials Used in Pyrotechnic Compositions" 1963; Shimizu, Chemical Components of Fireworks Compositions 2004).

OXIDIZING AGENTS

REQUIREMENTS

Oxidizing agents are usually oxygen-rich ionic solids that decompose at moderate-to-high temperatures, liberating oxygen atoms in some form. These materials must be readily available in a reasonably pure form, in the proper particle size, and at reasonable cost. They should give a neutral reaction when wet, be stable over a wide temperature range (or at least up to 100°C), and yet readily decompose to release oxygen at higher temperatures. For the pyrotechnic chemist's use, acceptable species include a variety of negative ions (anions), usually containing high-energy Cl–O or N–O bonds:

NO_3^- nitrate ion	ClO_3^- chlorate ion
ClO_4^- perchlorate ion	CrO_4^{2-} chromate ion
O^{2-} oxide ion	$Cr_2O_7^{2-}$ dichromate ion

The positive ions used to combine with these negatively charged anions must form stable, neutral compounds meeting several restrictions (Shidlovskiy 1964):

1. The oxidizer must be quite low in *hygroscopicity*, which is the tendency to acquire moisture from the atmosphere. Water can cause a variety of problems in pyrotechnic mixtures, and materials that readily pick up water are usually avoided. Hygroscopicity correlates well with the size and charge of the positive ions that makes up an ionic oxidizer. Li^+, Na^+, Mg^{2+}, and Al^{3+} are small ions that are often associated with hygroscopic compounds. Consequently, sodium salts (such as sodium nitrate—$NaNO_3$) are not often employed in pyrotechnics. Lithium, magnesium, and aluminum salts are similarly avoided due to their high hygroscopicity. Potassium salts tend to have lower hygroscopicity and are more commonly used in pyrotechnics. Hygroscopicity tends to parallel water solubility, and solubility data can be used to anticipate possible moisture-attracting problems. The water solubility of the common oxidizers can be found in Table 3.2. However, it should be mentioned that large quantities of sodium nitrate *are* used by the military in combination with magnesium metal for bright white light production and illumination. In order to use sodium nitrate, however, strict humidity controls are required throughout the manufacturing process to avoid moisture uptake, and the finished items must be sealed to prevent water from being picked up during storage. Only with strict manufacturing controls, along with effective packaging, can the unique light-producing properties of the sodium nitrate/magnesium system be exploited (see Chapter 10).

TABLE 3.2
Common Oxidizers and their Properties

Compound	Formula	Formula Weight	Melting Point, °C	Water Solubility, g/100 mL @ 20°C[a]	Heat of Decomposition, kcal/mol	Heat of Formation, kcal/mol[a]	Grams of Oxygen Released per Gram of Oxidizer	Weight of Oxidizer Required to Evolve One Gram of Oxygen
Ammonium nitrate	NH_4NO_3	80.0	170	118 (0°C)	–	−87.4	0.60 (total 0)	–
Ammonium perchlorate	NH_4ClO_4	117.5	Decomposes	37.2[c]	–	−70.6	~0.28	~3.5
Barium chlorate	$Ba(ClO_3)_2{\cdot}H_2O$	322.3	414	27 (15°C)	−28[b]	−184.4	0.32	3.12
Barium chromate	$BaCrO_4$	253.3	Decomposes	0.0003 (16°C)	–	−345.6	0.095	10.6
Barium nitrate	$Ba(NO_3)_2$	261.4	592	8.7	+104[b]	−237.1	0.31	3.27
Barium peroxide	BaO_2	169.3	450	Very slight	+17[b]	−151.6	0.09	10.6
Iron(III) oxide (red)	Fe_2O_3	159.7	1,565	Insol.	–	−197.0	0.30	3.33
Iron(II,III) oxide (black)	Fe_3O_4	231.6	1,594	Insol.	+266[b]	−267.3	0.28	3.62
Lead chromate	$PbCrO_4$	323.2	844	Insol.	–	−218	0.074	13.5
Lead dioxide (lead peroxide)	PbO_2	239.2	290 (decomposes)	Insol.	–	−66.3	0.13 (total 0)	7.48
Lead oxide (litharge)	PbO	223.2	886	0.0017	–	−51.5	0.072 (total 0)	14.0
Lead tetroxide (red lead)	Pb_3O_4	685.6	500 (decomposes)	Insol.	–	−171.7	0.093 (total 0)	10.7

(*Continued*)

TABLE 3.2 (*Continued*)
Common Oxidizers and their Properties

Compound	Formula	Formula Weight	Melting Point, °C	Water Solubility, g/100 mL @ 20°C[a]	Heat of Decomposition, kcal/mol	Heat of Formation, kcal/mol[a]	Grams of Oxygen Released per Gram of Oxidizer	Weight of Oxidizer Required to Evolve One Gram of Oxygen
Potassium chlorate	$KClO_3$	122.6	356	7.1	−10.6[c]	−95.1	0.39	2.55
Potassium nitrate	KNO_3	101.1	334	31.6[c]	+75.5[b]	−118.2	0.40	2.53
Potassium perchlorate	$KClO_4$	138.6	610	1.7[c]	−0.68[c]	−103.4	0.46	2.17
Potassium periodiate	KIO_4	230.0	582 (decomposes)	0.51	+33.29[d]	−111.7	0.28	3.57
Sodium nitrate	$NaNO_3$	85.0	307	92.1 (25°C)[c]	−111.8	−111.8	0.47	2.13
Sodium periodate (anhydrous)	$NaIO_4$	213.9	300	0.51	+33.8[d]	−102.6	0.30	3.34
Strontium nitrate	$Sr(NO_3)_2$	211.6	570	70.9 (18°C)	−233.8	−233.8	0.38	2.63

[a] Weast (1994).

[b] Shidlovskiy (1964).

[c] Shimizu (2004).

[d] Brusnahan, et al. (2017).

2. The oxidizer's positive ion (cation) must not adversely affect the desired flame color. Sodium, for example, is an intense emitter of yellow–orange light, and its presence can ruin attempts to generate red, green, and blue flames.
3. The alkali metals (Li, Na, K) and alkaline earth metals (Ca, Sr, and Ba) are preferred for the positive ion. These species are poor electron acceptors (and conversely, the metals are good electron donors), and they will not react in storage with active metal fuels such as Mg and Al. If easily reducible metal ions such as lead (Pb^{2+}) and copper (Cu^{2+}) are present in oxidizers, there is a strong possibility that a reaction such as:

$$Cu(NO_3)_2 + Mg \rightarrow Cu + Mg(NO_3)_2 \tag{3.2}$$

   will occur over time, especially under moist conditions, replacing the energetic magnesium fuel with less reactive copper metal. The pyrotechnic performance will be greatly diminished, and spontaneous ignition might occur as the replacement reaction proceeds exothermically.
4. The compound must have an acceptable heat of decomposition (the overall heat of reaction when a compound is decomposed into its elements or neutral species). A value that is too exothermic may produce explosive or highly sensitive mixtures, while a value that is too endothermic will cause ignition difficulties, as well as poor propagation of burning. For an oxidizer such as iron(III) oxide, Fe_2O_3, with a large, endothermic heat of decomposition, reaction will not occur with moderate-energy fuels like sulfur and sugar. A highly energetic fuel like magnesium, aluminum, or zirconium is required to extract the oxygen from iron oxide, leaving molten iron as a reaction product.
5. The compound should have as high an active-oxygen content as possible. Light cations (Na^+, K^+, NH_4^+) are desirable, while heavy cations (Pb^{2+}, Ba^{2+}) should be avoided if possible. Oxygen-rich anions, of course, are preferred. Notice the trade-off here with hygroscopicity—light positive ions tend to be hygroscopic and heavy cations reduce the active-oxygen content. Logic says to shoot for the elements with medium atomic weights for use as the cation in an oxidizer.
6. Finally, all materials used in high-energy compositions should be low in toxicity and yield low-toxicity reaction products, and—for all compositions developed in the 21st century—be environmentally "green."

In addition to ionic solids, covalent molecules containing halogen atoms (primarily F and Cl) can function as "oxidizers" in pyrotechnic compositions, especially with active metal fuels. Examples of this are the use of hexachloroethane (C_2Cl_6) with zinc metal in white smoke compositions,

$$3Zn + C_2Cl_6 \rightarrow 3ZnCl_2 + 2C \tag{3.3}$$

and the use of Teflon® (polytetrafluoroethylene) with magnesium metal in heat-producing, infrared-emitting mixtures dubbed "MagTef",

$$(C_2F_4)_n + 2n\ Mg \rightarrow 2n\ C + 2n\ MgF_2 + \text{heat/IR emission} \qquad (3.4)$$

In both examples for Equations 3.3 and 3.4, the metal has been "oxidized"—has lost electrons and increased in oxidation number—while the carbon atoms have gained electrons and been "reduced." Table 3.2 lists some of the common oxidizers together with a variety of their properties.

While there exists a large catalog of specialty oxidizers available for both military and civilian pyrotechnics, several common oxidizers are so widely used that they merit special consideration.

POTASSIUM NITRATE (KNO_3)

The oldest solid oxidizer used in high-energy mixtures, potassium nitrate (or saltpeter, as it was known for many years) remains a widely used ingredient into the 21st century. Its advantages are ready availability of high-purity material at reasonable cost, low hygroscopicity, and the relative ease of ignition of many mixtures prepared using it. The ignitability is related to the low (334°C) melting point of saltpeter. It has a high (39.6%) active oxygen content and decomposes at high temperature according to the equation:

$$2KNO_3 \rightarrow K_2O + N_2 + 2.5O_2 \qquad (3.5)$$

Notably, this is a strongly *endothermic* reaction—the reaction takes in heat instead of releases it—with a heat of decomposition value of +75.5 kcal/mol of KNO_3; consequently, high-energy output fuels must be used with saltpeter to achieve rapid-burning rates. When mixed with a simple organic fuel such as lactose, potassium nitrate may burn with some difficulty and stop at the potassium nitrite (KNO_2) stage in its decomposition (Shimizu, Fireworks—*The Art, Science and Technique* 1981).

$$KNO_3 \rightarrow KNO_2 + 1/2O_2 \qquad (3.6)$$

With good fuels (such as charcoal and active metals), potassium nitrate will react well. Potassium nitrate has the additional property of not undergoing an explosion/detonation by itself the same way that ammonium nitrate (NH_4NO_3) is known to do, even when very strong initiating modes are used (Shimizu, Fireworks—*The Art, Science and Technique* 1981).

POTASSIUM CHLORATE ($KClO_3$)

One of the most reactive, and certainly the most controversial, of the common oxidizers is potassium chlorate, $KClO_3$. It is a white, crystalline material of low hygroscopicity, with 39.2% oxygen by weight. It is prepared by electrolysis from a chloride salt in an energy-absorbing process—this energy input during manufacturing provides a means of storing energy in the oxidizer, for subsequent release during reaction with a fuel.

Potassium chlorate was used in the first successful colored-flame compositions in the mid-1800s and it remains in use today in colored-smoke compositions, firecrackers, toy pistol caps, matches, and some color-producing fireworks.

However, potassium chlorate has been involved in a number of serious accidents at fireworks manufacturing plants, and it must be treated with great care if it is used at all. Other oxidizers are strongly recommended over this material, if one can be found that will produce the desired pyrotechnic effect.

Potassium chlorate compositions are quite prone to accidental ignition, especially if sulfur, an acidic component, or even a small acidic impurity is also present. Chlorate–phosphorus mixtures are so sensitive and reactive that they can only be safely worked with when wet. The high hazard of $KClO_3$ mixtures was gradually recognized in the late 19th century, and England banned all chlorate–sulfur compositions in 1894. United States factories have greatly reduced their use of potassium chlorate as well, replacing it with the less-sensitive potassium perchlorate ($KClO_4$ instead of $KClO_3$) in many formulas. The Chinese, however, continue to use potassium chlorate in firecracker and some color compositions due to its unique properties and active pyrotechnic character.

Several factors contribute to the instability of potassium chlorate-containing compositions. The first is the low (356°C) melting point and low decomposition temperature of the oxidizer. Soon after melting, $KClO_3$ stoichiometrically decomposes according to the following net equation:

$$2KClO_3 \rightarrow 2KCl + 3O_2 \tag{3.7}$$

This reaction is quite vigorous and becomes violent at temperatures above 500°C (Shimizu, Fireworks—*The Art, Science and Technique* 1981). The actual decomposition mechanism may be more complex than Equation 3.7 initially suggests. Intermediate formation of potassium perchlorate has been reported at temperatures just above the melting point, with the perchlorate then decomposing to yield potassium chloride and oxygen (Ellern 1968). The involvement of the chlorite $\left(ClO_2^-\right)$ ion and radical has also been suggested (Stanbridge 1988).

$$4KClO_3 \rightarrow 3KClO_4 + KCl$$

$$3KClO_4 \rightarrow 3KCl + 6O_2$$

$$\text{Net:}\quad 4KClO_3 \rightarrow 4KCl + 6O_2$$

The decomposition reaction of potassium chlorate is rare among the common oxidizers because it is *exothermic*, with a heat-of-reaction value of approximately −10.6 kcal/mol (Shimizu, Fireworks—*The Art, Science and Technique* 1981). While most other oxidizers require a net heat input for their decomposition, potassium chlorate dissociates into KCl and O_2 with the *liberation* of heat. This heat output can then lead to rate acceleration and allows the ignition of potassium chlorate-containing compositions with a minimum of external energy input (ignition stimulus). In addition, potassium chlorate is capable of sustaining propagation of burning with low-energy fuels, at low temperatures, or under conditions of poor stoichiometry where other oxidizers (iron oxide, Fe_2O_3, for example) would not sustain the reaction.

A noted above, potassium chlorate is particularly sensitive when mixed with sulfur, a low-melting (119°C) fuel. It is also sensitive when combined with low-melting organic compounds, and low ignition temperatures are observed for most such compositions. Higher ignition temperatures are found for $KClO_3$–metal mixtures, attributable to the higher melting points, oxide coatings, and rigid crystalline lattices of these metallic fuels. However, these mixtures can be quite sensitive to ignition by spark or friction (see Chapter 7) because of their substantial heat output and should still be regarded as quite hazardous. Ignition temperatures for some $KClO_3$ mixtures are given in Table 3.3. It should be noted, and is discussed later, that ignition temperatures are quite dependent upon the experimental and material conditions; a range of ±50°C may be observed, depending on sample size, heating rate, degree of confinement, and the experimental method that is used (Barton 1982).

Mixtures containing potassium chlorate can be quite susceptible to the presence of a variety of chemical species. Acids can have a dramatic effect: The addition of a drop of concentrated sulfuric acid (H_2SO_4) to most $KClO_3$–fuel mixtures results in immediate ignition of the composition. This dramatic reactivity has been attributed to the formation of chlorine dioxide (ClO_2) gas, a powerful oxidizer (Ellern 1968). The presence of basic "neutralizers" such as magnesium carbonate and sodium bicarbonate in $KClO_3$ mixtures can reduce the sensitivity of chlorate-containing compositions to trace amounts of acidic impurities.

The ability of a variety of metal oxides—most notably manganese dioxide (MnO_2) to catalyze the thermal decomposition of potassium chlorate into potassium chloride and oxygen has been known for years. Little use is made of this behavior in pyrotechnics, however, because $KClO_3$ is almost *too* reactive in its normal state and ways are not needed to *enhance* its reactivity. Materials and methods to retard its decomposition are desired instead. However, knowledge of the ability of many materials to accelerate the decomposition of $KClO_3$ suggests that *impurities* could be quite an important factor in determining the reactivity and sensitivity of chlorate-containing mixtures. It is vitally important that the $KClO_3$, as well as all other components blended with $KClO_3$ that are used in pyrotechnic manufacturing operations, be of the highest possible purity, and that all possible precautions must be taken in storage and handling to prevent contamination of the material.

TABLE 3.3
Ignition Temperatures of Potassium Chlorate/Fuel Mixtures

Fuel	Ignition Temperature of Stoichiometric Mixture with $KClO_3$, °C[a]
Lactose, $C_{12}H_{22}O_{11}$	195
Sulfur	220
Shellac	250
Charcoal	335
Magnesium powder	540
Aluminum powder	785
Graphite	890

[a] Shidlovskiy (1964).

McLain has reported that potassium chlorate containing 2.8 mol% copper chlorate as an intentionally added impurity (or "dopant") reacted explosively with sulfur at room temperature (McLain 1980)! A pressed mixture of potassium chlorate with "realgar" (arsenic sulfide, As_2S_2) has also been reported to ignite at room temperature (Shimizu, Chemical Components of Fireworks Compositions 2004).

A study by Conkling and Halla investigated the relationship between the melting point of an organic fuel and the ignition temperature of a stoichiometric mixture of that compound with potassium chlorate. The results indicated that the onset of ignition was triggered by the thermal *decomposition* of the fuel, rather than by its melting point. A low decomposition temperature for a carbon-based compound should correspond with an increased tendency for that compound to readily undergo oxidation, if oxygen is available. Sugars, which tend to decompose at their melting points, were found to form mixtures with potassium chlorate that ignited at the melting/decomposition temperature of the sugar, suggesting that it might be possible to formulate mixtures with specific ignition temperatures. Carbon compounds such as benzoic acid, with stable liquid phases, ignited at higher temperatures corresponding to their decomposition temperatures in the liquid state (Conkling and Halla 1984).

Ammonium chlorate, NH_4ClO_3, is an *extremely* unstable compound that decomposes violently at temperatures well below 100°C. If a mixture containing both potassium chlorate and an ammonium salt is prepared, there is a good possibility that an exchange reaction will occur—especially in the presence of moisture or catalytic metals such as copper, to form some of the ammonium chlorate:

$$NH_4X + KClO_3 \xrightarrow{H_2O} NH_4ClO_3 + KX\left(X = Cl^-, NO_3^-, ClO_4^-, \text{etc.}\right)$$

If this reaction occurs, the chance of spontaneous ignition of the mixture is likely. Therefore, any composition containing both a chlorate salt and an ammonium salt must be considered extremely hazardous. The shipping regulations of the United States Department of Transportation classify any such mixtures as "forbidden explosives" because of their instability (U.S. Department of Transportation n.d.). It should be noted, however, that compositions consisting of potassium chlorate, ammonium chloride (NH_4Cl), and organic fuels have been used, reportedly safely, for white smoke production (Shimizu, Fireworks—*The Art, Science and Technique* 1981).

Colored-smoke compositions represent a major use of potassium chlorate, and the safety record of these mixtures is excellent. An acid neutralizer (e.g., $MgCO_3$ or $NaHCO_3$) is typically added for storage stability, as well as to lower the overall reaction temperature through an endothermic decomposition, in the flame, of the type:

$$MgCO_3 \xrightarrow{\text{Heat}} MgO + CO_2$$

This reaction helps "soak up" excess heat in the reaction that might otherwise decompose the colored dye and denature the coloring property (see Chapter 11). The carbon dioxide gas that forms during the decomposition also aids in dispersing the volatile smoke dyes. Thus, the magnesium carbonate (or sodium bicarbonate) is playing three important roles in the performance and stability of the smoke composition—acid neutralizer, coolant, and smoke disperser.

Colored-smoke mixtures also contain either sulfur or a carbohydrate as the fuel, and a volatile organic dye that sublimes from the reaction mixture to produce the colored smoke. These compositions contain a large excess of potential fuel, and their explosive properties are greatly diminished as a result. Smoke mixtures must react with low flame temperatures (500°C or less, depending on the dye that is used) or the complex dye molecules will decompose, as noted above, producing black soot instead of a brilliantly colored smoke. Potassium chlorate is far and away the best oxidizer for use in these compositions.

Potassium chlorate is truly a unique material. Shimizu has stated that no other oxidizer can surpass it for burning speed, ease of ignition, or noise production using a minimum quantity of composition (Shimizu, Fireworks—*The Art, Science and Technique* 1981). It is also among the very best oxidizers for producing colored flames, with ammonium perchlorate as its closest rival. Chlorate-containing compositions can be prepared, by altering the fuel and the fuel–oxidizer ratio that will ignite and propagate at a wide range of reaction rates and flame temperatures for use in applications ranging from colored-smoke mixtures to colored-flame formulations to high-temperature flash compositions. $KClO_3$ is a versatile material, but the inherent dangers associated with it require that alternate oxidizers be employed wherever possible. It is just *too* unstable and unpredictable to be safely used by the pyrotechnician in anything but colored-smoke compositions, and even then, both coolants and considerable care are required!

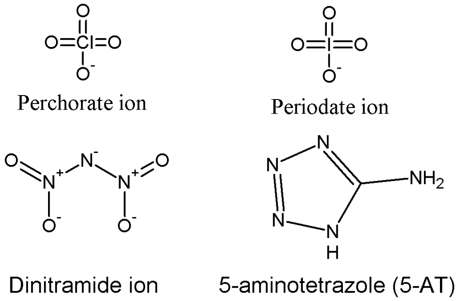
POTASSIUM PERCHLORATE ($KClO_4$)

The material potassium perchlorate, with one extra oxygen, gradually replaced potassium chlorate ($KClO_3$) as the principal oxidizer in civilian pyrotechnics during the 20th century. Its safety record is far superior to that of potassium chlorate, although caution must still be used and a hazard analysis must still be conducted on all compositions and manufacturing processes, using sensitivity and output data, prior to scaling up production of any energetic material. Perchlorate mixtures, especially with a metal fuel such as aluminum, can have explosive properties, especially when present in bulk quantities and when confined. The chemical structure of the perchlorate ion is shown in Figure 3.1.

Potassium perchlorate is a white, non-hygroscopic crystalline material with a melting point of 610°C, considerably higher than the 356°C melting point of $KClO_3$. It undergoes decomposition at high temperature:

$$KClO_4 \overset{\text{Heat}}{\rightarrow} KCl + 2O_2$$

forming potassium chloride and oxygen gas. This reaction has a slightly exothermic value of −0.68 kcal/mol and produces substantial oxygen (Military Pyrotechnic Series Part Three: "Properties of Materials Used in Pyrotechnic Compositions" 1963). The 46.2% active oxygen content of $KClO_4$ is one of the highest available to the pyrotechnician.



Perchorate ion

Periodate ion

Dinitramide ion

5-aminotetrazole (5-AT)

FIGURE 3.1 Molecular structures of the perchlorate ion $\left(ClO_4^-\right)$, periodiate ion $\left(IO_4^-\right)$, dinitramide ion $\left(N_3O_4^-\right)$, and 5-aminotetrazole (CH_3N_5). Perchlorate ions are taken into the human body and are inadvertently treated as an iodide (I^-) ion, which can cause thyroid malfunction and other issues. Three notable potential replacements for use of perchlorates (such as potassium perchlorate or ammonium perchlorate) are periodates, which replace chlorine with a similar halogen iodine in the ion, dinitramides for use in propellants, and the high-nitrogen-content 5-aminotetrazole (neutral organic molecule). Both periodates and 5-aminotetrazole have shown some utility in colored-flame production, which has previously relied heavily on perchlorates for both oxidation utility and as a chlorine donor, discussed in detail in Chapter 10.

Because of its higher melting point and less-exothermic decomposition, potassium perchlorate typically produces mixtures that are less sensitive to heat, friction, and impact than those made with $KClO_3$ (Shimizu, Fireworks—*The Art, Science and Technique* 1981). Potassium perchlorate can be used to produce colored flames (such as red when combined with strontium nitrate), noise (with aluminum, in "flash and sound" mixtures), and light (in photoflash mixtures with magnesium). It also makes an excellent, but very spark-sensitive, ignition composition, "ZPP," when blended with zirconium.

GREEN PYROTECHNICS: THE PERCHLORATE ISSUE

When the first edition of this book was published in 1985, a widely held opinion among pyrotechnicians was that potassium perchlorate was the "ideal" oxidizer to use in energetic pyrotechnic compositions, and potassium nitrate was the first choice for moderately energetic systems. Similarly, ammonium perchlorate was viewed as an "ideal" oxidizer for propellant formulations, producing all gaseous products in its thermal decomposition.

The positive features of the perchlorate oxidizers were reasonable cost, acceptable hygroscopicity, good stability, and low toxicity, as well as availability in high purity in a wide range of particle sizes, along with excellent reactivity with a wide range of fuels. The two perchlorate oxidizers (ammonium and potassium) were widely used for a number of decades in solid rocket propellants, signal flare compositions, explosive simulators, and an assortment of other pyrotechnic applications. The fireworks manufacturing industry significantly improved its safety record as color compositions made with potassium chlorate were replaced by less sensitive and more stable potassium perchlorate formulations.

However, the excellent stability of the perchlorates—one of their strongest selling points for use in energetic compositions—has also become a great weakness for these oxidizers. Studies have indicated that perchlorate oxidizers are quite sluggish in their reaction at ambient temperatures with typical fuels (organic matter) that are found in the environment, and they appear to have considerable persistence in soil and ground water. Some microorganisms do appear to be capable of metabolizing the perchlorate ion, and research in this area continues.

The concern with perchlorates involves studies that have linked the perchlorate ion, even in low concentrations, to thyroid disorders. The perchlorate ion appears to be an ideal substitute, in size and charge (–1) for the iodide ion (I^-). Consumption of water containing perchlorate ion appears to lead to incorporation of the perchlorate ion by acceptor sites in the thyroid gland, replacing the biologically active iodide ion, thereby possibly creating developmental problems in pregnant women and young children (Sellers and et al. 2007).

The good news here appears to be that the effect appears to be preventable and reversible. The intake of foods and beverages with iodide content appears to lead to a replacement of the perchlorate ion with iodide, and this should be particularly beneficial if the supply of water that contains perchlorate is replaced with perchlorate-free material. Research into this issue is ongoing, but the issue has led manufacturers of both military and civilian devices containing perchlorate oxidizers to seek replacement materials. This has proven to be possible in some systems, and a real challenge in others, without resorting back to the use of the hazardous chlorate oxidizers.

One thing we do know if that the perchlorate ion converts in what should be a nearly quantitative manner back to the much more environmentally acceptable chloride ion upon ignition of an energetic composition, such as the reaction

$$3KClO_4 + 8Al \rightarrow 3KCl + 4Al_2O_3 \tag{3.8}$$

that takes place with a flame temperature in the 3,000°C range. If perchlorate-containing compositions ignite and function properly, the use of perchlorate oxidizers is of far less concern with respect to environmental contamination.

Obviously, then, the major opportunity for ground contamination with perchlorate occurs at manufacturing sites. As a result, manufacturers of propellants and pyrotechnics have proceeded to take appropriate measures and institute “best management practices” to prevent the release of perchlorate materials into groundwater systems, while research is underway to find replacement formulations that are perchlorate-free, as well as to better determine hazardous exposure levels for humans (Sellers and et al. 2007).

Both military and civilian/commercial research projects have been undertaken to determine which, if any, oxidizers can be used instead of perchlorate that can provide similar performance at similar costs, notably in propellant and colored-flame compositions. Dinitramide salts $\left(N_3O_4^-\right)$ have been suggested as replacements for perchlorates in propellants. Work undertaken by Sabatini and Moretti et al. published in the 2013–2014 timeframe describes several studies, including investigating periodate $\left(IO_4^-\right)$ salts instead of perchlorates for incendiary formulations (Moretti, Sabatini and Chen, Periodate Salts as Pyrotechnic Oxidizers: Development of Barium- and Perchlorate-Free Incendiary Formulations 2012), the use of oxidizers based on 5-aminotetrazole, instead of perchlorate, in red- and green-light formulations (Sabatini and Moretti 2013), and further work on red-light-emitting strontium-based formulations without the use of perchlorate (Moretti, Sabatini and Poret, "High-Performing Red-Light-Emitting Pyrotechnic Illuminants Through the Use of Perchlorate-Free Materials" 2014). Interestingly, *chlorate* is also being investigated as a replacement for perchlorate oxidizers, even noting some of the safety considerations discussed earlier (Railbeck, Kislowski and Chen 2008); generally, these chlorate-for-perchlorate formulations contain some amount of coolant, such as magnesium carbonate, to moderate the heat output. Several perchlorate-replacement studies are outlined later in this chapter, and in subsequent chapters, for specific compositions.

AMMONIUM PERCHLORATE (NH_4ClO_4)

The "newest" oxidizer to appear in significant use in pyrotechnics, ammonium perchlorate or "AP", has found considerable use in modern solid-fuel rocket propellants and in the fireworks industry. The now-retired NASA Space Shuttle alone used approximately 2 million pounds of solid fuel per launch; the mixture is 70% ammonium perchlorate, 16% aluminum metal, and 14% organic polymer/epoxy, with a trace of iron oxide catalyst that can be varied to modify the burn rate (NASA—Solid Rocket Boosters 2006). The aluminum powder is a surprising ingredient to find in a propellant, since it generates *solid* particles, rather than the gaseous reaction products usually desired in propellants; but, the substantial heat output of aluminum as a fuel, and its excellent thermal conductivity, contribute to an enhancement of the burn rate of this propellant formulation and made it ideal for the launch.

Ammonium perchlorate undergoes a complex chemical reaction on heating, with decomposition occurring over a wide range, beginning near 200°C. Decomposition occurs prior to melting, so a liquid state is not produced—the solid starting material goes directly to gaseous decomposition products. The decomposition position reaction is reported by Shimizu (Shimizu, Fireworks—*The Art, Science and Technique* 1981) to be

$$2NH_4ClO_4 + \text{heat} \rightarrow N_2 + 3H_2O + 2HCl + 2.5O_2 \tag{3.9}$$

This equation corresponds to the evolution of 80 g (2.5 mol) of oxygen gas per 2 mol (235 g) of NH_4ClO_4, giving an "active oxygen" content of 34% (versus 39.2% for $KClO_3$ and 46.2% for $KClO_4$). The fact that AP generates all gaseous products makes it a valuable material for propellant formulations or compositions where little to no solid products are desired. The decomposition reaction, above 350°C, is reported to be considerably more complex (Military Pyrotechnic Series Part One, "Theory and Application" 1967).

$$\begin{aligned}10NH_4ClO_4 \rightarrow\ & 2.5Cl_2 + 2N_2O + 2.5NOCl + HClO_4 \\ & + 1.5HCl + 18.75H_2O + 1.75N_2 + 6.38O_2\end{aligned} \tag{3.10}$$

Mixtures of ammonium perchlorate with fuels can produce high flame temperatures when ignited, and the hydrogen chloride (HCl) liberated during the reaction can aid in the production of colors. These two factors make ammonium perchlorate a good oxidizer for colored-flame composition (see Chapter 10).

Ammonium perchlorate is more hygroscopic than potassium nitrate or potassium chlorate, and some precautions should be taken to keep mixtures dry. The hygroscopicity problem can be substantial if a given composition also contains potassium nitrate or even comes in contact with a potassium nitrate-containing mixture. Here, the exchange reaction

$$NH_4ClO_4 + KNO_3 \xrightarrow{H_2O} KClO_4 + NH_4NO_3$$

can occur, especially in the presence of moisture. The exchange product, ammonium nitrate (NH_4NO_3) is very hygroscopic, and ignition problems may well develop over time (Shimizu, Fireworks—*The Art, Science and Technique* 1981). Also, ammonium perchlorate should not be used in combination with a chlorate-containing compound as noted previously, due to the possible formation of unstable (spontaneously explosive!) ammonium chlorate in the presence of moisture.

Magnesium metal should also be avoided in ammonium perchlorate compositions. Here the reaction

$$2NH_4ClO_4 + Mg \rightarrow 2NH_3 + Mg(ClO_4)_2 + H_2 + \text{heat} \tag{3.11}$$

can occur in the presence of moisture due to the weakly acidic nature of ammonium perchlorate. Spontaneous ignition may occur if the heat buildup is substantial.

Under particularly severe initiation conditions, ammonium perchlorate can be made to explode by itself (Price, Clairmont, and Jaffee 1967). It appears to be difficult to get ammonium perchlorate to detonate on its own, with a shock stimulus (as opposed to heat) needed to get the pure material to explode. Mixtures of ammonium perchlorate with sulfur and antimony sulfide are reported to be considerably more shock-sensitive than comparable potassium chlorate compositions (Shimizu, Fireworks—*The Art, Science and Technique* 1981). Fine ammonium perchorate (largely 1–5 μm in number) mixed with fine aluminum powder (3–25 μm in size) can detonated, while coarser ammonium perchlorate produces compositions that deflagrate under the same initiation conditions (Tulis and et al. 1986). Ammonium perchlorate compositions, ignited by flame, can be used to produce excellent flame colors with little solid residue, but care must be exercised always with this oxidizer. The explosive potential of this material suggests that minimum amounts of bulk energetic composition should be prepared at one time, and large quantities should not be stored at manufacturing sites.

AMMONIUM PERCHLORATE IN THE NEWS

Prior to the perchlorate environmental concerns making the news, ammonium perchlorate (AP) was involved in another news-worthy event (Sellers and et al. 2007). An explosion in 1988 arising from a fire at an ammonium perchlorate manufacturing facility near Henderson, Nevada, produced measurable property damage over a wide area and reemphasized the energetic nature of ammonium perchlorate (Reed 1992; Seltzer 1998). This has been referred to as the "PEPCON Disaster," so named for the Pacific Engineering and Production Company of Nevada.

Approximately 8 million pounds of AP was stored on-site in 500- and 5,000-pound containers.[2] A fire began in the manufacturing area during routine maintenance operations and quickly spread through the entire facility. At some point during the event, a natural gas line beneath the plant ruptured as well, adding "fuel to the fire" and making analysis of the event even more complex. Several smaller blasts were followed by a major explosion that registered on seismographs all over the western United States.

The investigation that followed after the event revealed the large quantity of ammonium perchlorate that was in storage at the facility, awaiting shipment to the solid propellant manufacturing industry. Fortunately, the emergency response system worked exceptionally well, and the event was limited to a single fatality. Further research ultimately developed the modern standard that AP in fine particle size (15 μm and under) should be treated as a high explosive (1.1 material) for transportation, while it can be transported as a Class 5 oxidizer in larger particle sizes (U.S. Department of Transportation n.d.).

DINITRAMIDES: A "GREEN" REPLACEMENT FOR PERCHLORATES?

There is some interest in "dinitramide" molecules, based on the anion $N_3O_4^-$, most commonly in the salts ammonium dinitramide "ADN" or potassium dinitramide "KDN." It has been reported that ADN can be a viable replacement for ammonium perchlorate-based solid rocket fuels without the chlorine-containing products—unreacted perchlorate and hydrogen chloride gas products—that could be harmful in the environment (Venkatachalam, Santhosh, and Ninan 2004). Ammonium dinitramide, ideally, will produce only water and nitrogen gas as reaction products.

From a safety standpoint, however, dinitramide salts tend to have much lower melting temperatures than perchlorate salts: potassium dinitramide melts at 128°C, versus potassium perchlorate at 356°C, and ammonium dinitramide melts at 93°C (less than the boiling point of water!) versus ammonium perchlorate decomposing—not melting—around 200°C. This can be both a benefit for rapid burning (propellants) as well as a safety hazard for storage and handling, not to mention an economic consideration for decomposition over time in storage. Research in this area is ongoing, but studies by Larsson and Wingborg in the Swedish Defence Research Agency find that ADN is a promising "green" substitute for AP as well as the highly toxic and unstable (but popular in military and aerospace applications) hydrazine, N_2H_4 (Larsson and Wingborg 2011).

While the availability and cost of these salts may still preclude the everyday pyrotechnician from switching out perchlorates for dinitramides, large-scale propellant, commercial, and military applications (that measure oxidizer usage in the *tons* and not grams) may have interest in these materials as more environmentally benign oxidizers.

The structure of the dinitramide ion is shown in Figure 3.1.

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[2] The large amount stored at this site resulted from the Space Shuttle program's need for large amounts of AP-based solid rocket propellant, which PEPCON supplied.

PERIODATES: A "GREEN" REPLACEMENT FOR PERCHLORATES?

Recent research by several groups has studied how periodates $\left(IO_4^-\right)$ perform in pyrotechnic compositions as a possible replacement for the chlorine-based counterpart: perchlorates. Iodine, I, is another "halogen" that is one row down from chlorine on the periodic table. Periodates are also not expected to have the same thyroid interaction problems as perchlorates. Both potassium periodate (KIO_4) and sodium periodate ($NaIO_4$) have been studied as replacements for perchlorate oxidizers, mainly for illuminating colored-flame compositions, which will be discussed further in Chapter 10. Technical information on potassium and sodium periodates is listed in Table 3.2.

Periodates will not necessarily be a "drop in" replacement for perchlorates due to some notable differences. The overall decomposition of potassium perchlorate is exothermic (releasing heat upon decomposition to potassium chloride, KCl, and molecular oxygen gas), while the overall decomposition of sodium and potassium periodate (to sodium iodide and potassium iodide, respectively, along with molecular oxygen gas) are both *endothermic*. Potassium perchlorate, then, aids the ignition and propagation of a reaction by releasing more heat upon reaction, substantiating the burn rate, where periodates *consume* heat upon reaction, which may retard ignition or overall burn rate. A stronger fuel or other additives might be required with periodates as the oxidizer to mitigate this difference. However, the melting/decomposition points of periodates are lower than that of potassium perchlorate, so overall ignition temperatures might be lower in compositions that replace perchlorates with periodates. Both of these effects—an endothermic decomposition but lower melting temperature for periodates—should be considered when developing a new composition.

Some drawbacks of periodates include potassium periodiate's incompatibility with tungsten metal in the presence of moisture, forming potassium tungstate (K_2WO_4) and releasing elemental iodine, I_2 (Brusnahan, et al. 2017). A brief review of pricing at the time of this writing also finds that potassium periodate is over three times as expensive in bulk form as potassium perchlorate, with no common pyrotechnic chemical suppliers stocking the chemical for hobbyist fireworks use; only larger industrial chemical suppliers were listing potassium periodate for sale, often in extremely pure laboratory-grade forms, as periodates are common organic-synthesis reactants. This cost excess may be due to the production process for periodate, which requires a two-step electrochemical synthesis from iodine to iodate, IO_3^-, with further oxidation to the final periodate.

The toxicity of periodates has also not been studied to the same degree as perchlorates, the latter of which are known to affect the thyroid gland. Some studies are underway on the acute toxicity of periodates, which find that periodates might be *more* acutely toxic by ingestion than perchlorates. However, it is noted that ingestion is not the expected exposure path (Brusnahan, et al. 2017).

The main use of periodates as replacement for perchlorates in pyrotechnics has been in the study of new "green pyrotechnics" illuminants and colored-flame compositions, which are discussed in more detail in Chapter 10. The structure of the periodate ion is shown in Figure 3.1.

5-AMINOTETRAZOLE: A "GREEN" REPLACEMENT FOR PERCHLORATES?

Recent research has shown that the high-nitrogen-content organic molecule 5-aminotetrazole—CH_3N_5—shows promise as a replacement for perchlorates, specifically in colored-flame production. Abbreviated as 5-AT, this compound is produced at an industrial scale (beneficial for cost considerations), has a negative heat of decomposition (releasing nitrogen gas as a decomposition product), is generally thermally stable, is minimally toxic, and produces a large amount of gas upon combustion (Han, et al. 2017). For this reason, 5-AT is also being investigated as a potential gas-generator component for airbags and smoke-generating systems. While at first it may seem strange that net *fuel* would be a replacement for the perchlorate oxidizer (pyro valence of 5-AT is +7, compared to potassium perchlorate of −8), most compositions employing 5-AT will use an additional oxidizer (such as a nitrate salt) that would normally not be suitable as a simple replacement for perchlorate.

Further use of 5-AT in specific systems is discussed in Chapters 10 and 11. The structure of 5-aminotetrazole is shown in Figure 3.1.

STRONTIUM NITRATE [$Sr(NO_3)_2$]

Strontium nitrate, before the "perchlorate issue" came to light, had rarely been used as the sole oxidizer in a pyrotechnic composition but was commonly combined with potassium perchlorate in red flame mixtures to generate the necessary activity and color output. Recently, however, with the "perchlorate issue," some work is being done on compositions with strontium nitrate as the sole oxidizer for red flame mixtures, with positive output results recorded (Sabatini and Moretti 2013).

Strontium nitrate is a white crystalline solid with a melting point of approximately 570°C. It is somewhat hygroscopic, so moisture should be avoided when using this material. Near its melting point, strontium nitrate decomposes according to

$$Sr(NO_3)_2 \rightarrow SrO + NO + NO_2 + O_2 \tag{3.12}$$

Strontium nitrite, $Sr(NO_2)_2$, is formed as an intermediate in this decomposition reaction, and a substantial quantity of the nitrite can be found in the ash of low flame temperature mixtures (Shimizu, Fireworks—*The Art, Science and Technique* 1981). At higher reaction temperatures, the full decomposition is

$$Sr(NO_3)_2 \rightarrow SrO + N_2 + 2.5O_2 \tag{3.13}$$

This is a strongly endothermic reaction, with a heat reaction of +92 kcal, and corresponds to an active oxygen content of 37.7%. Little ash is produced in the high-temperature process (mainly just strontium oxide), which occurs in mixtures containing magnesium or other "hot" fuels.

The standard red highway flare, or "fusee," typically uses a significant amount of strontium nitrate in its formulations, together with slow-burning fuels such as sulfur and common sawdust, in order to obtain the long burning times (up to 30 min) required for these devices. The challenge in producing this device is to obtain a trifecta of good candlepower/light intensity, a deep red flame color, *and* a slow burning time. Any two of these can be accomplished straightforwardly, but achieving all three takes just the right composition chemistry, bulk material properties, and packaging/confinement. The formulations of flare products that have all three attributes in good measure are often well-kept secrets.

BARIUM NITRATE [$Ba(NO_3)_2$]

Barium nitrate is a white, crystalline, non-hygroscopic material with a melting point of approximately 592°C. It is commonly used as the principal oxidizer in green-flame compositions, gold sparklers, and in photoflash mixtures in combination with potassium perchlorate. At high reaction temperatures, barium nitrate decomposes according to

$$Ba(NO_3)_2 \rightarrow BaO + 2.5O_2 \tag{3.14}$$

This reaction corresponds to 30.6% available oxygen. At lower reaction temperatures, barium nitrate produces nitrogen oxides (NO and NO_2) instead of nitrogen gas, as does strontium nitrate (Shimizu, Fireworks—*The Art, Science and Technique* 1981).

Mixtures containing barium nitrate as the sole oxidizer are typically characterized by higher ignition temperatures relative to potassium nitrate and potassium chlorate compositions. The higher melting point and decomposition temperature of barium nitrate are primarily responsible for these higher ignition values. Unfortunately, barium nitrate is known to have toxic effects such as irritating the skin, inflaming the respiratory tract, and can cause cardiac and muscle disorders (National Institues of Health 2018). In the "green pyrotechnics" effort, research is taking place into replacing barium nitrate compositions with other, less toxic oxidizers. Further discussion of how barium is being replaced by "greener" chemicals is discussed in Chapter 10.

IRON OXIDE [Fe_2O_3 AND Fe_3O_4]

"Red" iron oxide (hematite, Fe_2O_3) is used in certain mixtures where a high ignition temperature and a substantial quantity of molten solid products (and lack of gaseous product) are desired. For example, the "classic" thermite reaction,

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe \tag{3.15}$$

is an example of this type of system and can be used to do pyrotechnic welding and assorted other applications where a hot molten slag is desired. The melting point of Fe_2O_3 is 1,565°C, and the ignition temperature of thermite mix is above 800°C. When ignited, a reaction temperature of approximately 2,400°C is reached, and 0.93 kcal is evolved per gram of composition (Shimizu, Fireworks—*The Art, Science and Technique* 1981; Weast 1994). Because of its significantly endothermic heat of decomposition, +199 kcal/mol, iron oxide will only react with active, energetic fuels, almost always metals, such as Al, Si, B, or Zr. A mixture of iron oxide with sugar—a moderate organic fuel—will only produce rusty caramel if ignition of the mixture is attempted. There is not enough energy generated by the oxygen–sugar reaction to sustain the decomposition of the iron oxide, and the sugar will burn or caramelize well before the iron oxide is melted or in a state to donate its oxygen atoms to begin the pyrotechnic reaction.

"Black" iron oxide (magnetite, Fe_3O_4) is also used in certain mixtures where a high ignition temperature is desired. Black iron oxide has a similar melting temperature as red iron oxide at 1,597°C, with an even more endothermic heat of decomposition of +266 kcal/mol (Kosanke and Kosanke 2012). Black iron oxide can also be used in thermite reactions to similar effects:

$$3Fe_3O_4 + 8Al \rightarrow 4Al_2O_3 + 9Fe \tag{3.16}$$

Black thermite has a slightly lower enthalpy of reaction, with 0.85 kcal evolved per gram of composition (versus 0.93 kcal with red thermite) (Shidlovskiy 1964). Because it has a more endothermic heat of decomposition and evolves less heat per gram of thermite composition, red iron oxide is typically the oxidizer of choice for pyrotechnicians.

"Thermites" are a class of heat-producing, typically gas-less compositions where one metal fuel is oxidized, while another oxidized metal is reduced to its metallic (and during the hot reaction, molten) form. These are explored in depth in Chapter 8.

OTHER OXIDIZERS

A variety of other oxidizers are occasionally used in high-energy mixtures, generally with a specific purpose in mind for which chemists have found that particular, although less common, oxidizers have a more suitable purpose.

Barium chlorate—$Ba(ClO_3)_2$—for example, has been used in some green-flame compositions. These mixtures can be very sensitive, however, and great care must be used during mixing, loading, and storing.

Barium chlorate is interesting because it exists as a *hydrate* when crystallized from a water solution. It has the formula $Ba(ClO_3)_2 \bullet H_2O$. Water molecules are found in the crystalline lattice in a one-to-one ratio with barium ions. The molecular weight of the hydrate is 322.3 ($Ba + 2\ ClO_3 + H_2O$), so the water must be included in stoichiometry calculations. On heating, the water is driven off at 120°C, producing anhydrous $Ba(ClO_3)_2$, which later melts at 414°C. The thermal decomposition of barium chlorate is strongly exothermic (–28 kcal/mol). This value, greater than that of 1 mol of potassium chlorate, causes barium chlorate mixtures to be very sensitive to various ignition stimuli.

Other oxidizers—including barium chromate ($BaCrO_4$), lead chromate ($PbCrO_4$), sodium nitrate ($NaNO_3$), lead dioxide (PbO_2), lead tetroxide (Pb_3O_4), bismuth oxide (Bi_2O_3), copper oxide (CuO), and barium peroxide (BaO_2)—will also be encountered in subsequent chapters. Several novel or non-legacy oxidizers are being looked at as "green pyrotechnics" alternatives to perchlorates and barium-based compounds. One such example is potassium ferrate—K_2FeO_4—which decomposes to red iron oxide—Fe_2O_3—upon combustion but is susceptible to acidic conditions and will generally have a much lower burning temperature than potassium perchlorate it is intended to replace (Wilharm, Chin and Pliskin 2014).

Bear in mind that reactivity and ease of ignition are often related to the melting point of the oxidizer, and the volatility of the reaction products determines the amount of gas that will be formed from a given oxidizer–fuel combination. Table 3.2 contains the physical and chemical properties of some common oxidizers, and other, less-common oxidizers will be noted, as their use in various reactions is discussed in later chapters.

OXIDIZERS WITHOUT OXYGEN

Any oxygen-containing compound has the potential to serve as an oxidizer in an energetic mixture, provided that it is blended with a fuel that can provide sufficient energy upon oxidation to decompose the oxidizer and sustain the reaction. However, other electronegative elements can be used as oxidizers in similar situations as the oxygen atom might, recall Equations 3.3 and 3.4, above, using chlorine and fluorine, respectively, as oxidizers.

To point, Shidlovskiy notes that metal-fluorine compounds should have good oxidizer capability. For example, the reaction

$$FeF_3 + Al \rightarrow AlF_3 + Fe \tag{3.17}$$

is quite exothermic ($\Delta H = -70$ kcal/mol).[3] However, the lack of stable, economical metal fluorides of the proper reactivity has limited research in this direction (Shidlovskiy 1964).

SUMMARY ON OXIDIZERS AND THEIR USE

In summary, an oxidizer has two primary properties that determine its reactivity. One is its heat of decomposition, which indicates the amount of energy that must be supplied by the oxidation of a fuel in order to liberate oxygen for subsequent reaction with more fuel and achieve propagation of the reaction. The second property of interest is the melting point of the oxidizer, which is a good indication of the temperature that must be reached in order for oxygen to be readily liberated from the oxidizer.

An oxidizer with a low melting point and a weakly endothermic—or even better, an exothermic—heat of decomposition should be capable of reacting with a fuel under extremely poor conditions, such as in very cold environments and with low heat-output fuels. The classic example of this type of oxidizer is potassium chlorate, which can sustain combustion with poor fuels (such as sulfur or sucrose) under the most adverse conditions. On the other end of the reactivity scale, a combination of an active oxidizer with an energetic fuel, such as one of the active metal powders, will produce a *highly* reactive mixture and require great care in its preparation, handling, and use.

The other extreme for oxidizers will be those materials with highly endothermic heats of decomposition and high melting points, such as iron (III) oxide, Fe_2O_3. Such materials will require a highly exothermic fuel (such as magnesium, aluminum, or zirconium) in order for a reaction to occur.

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[3] Compare this iron-*fluorine* and aluminum composition to the "thermite" iron-*oxygen* and aluminum reactions noted previously; similar process, with the oxidizing atom being the difference.

A comparison of two oxidizers, potassium chlorate ($KClO_3$) and iron(III) oxide (Fe_2O_3—red iron oxide), shows the wide range of properties available for selection by a pyrotechnic formulator. Potassium chlorate will ignite and react with a wide range of fuels, while iron oxide requires a very energetic fuel in order for ignition and reaction to occur.

OXIDIZER SELECTION: A COMPARISON

	Potassium Chlorate, $KClO_3$	**vs.**	**Iron(III) Oxide, Fe_2O_3**
Melting point:	336°C		1,565°C
Heat of decomposition:	–10.6 kcal/mol		+199 kcal/mol

FUELS

REQUIREMENTS

In addition to an oxidizer, pyrotechnic mixtures will also contain one or more fuels, or electron donors, that react with the liberated oxygen from the oxidizer to produce an oxidized product plus heat. This heat will enable the high-energy chemist to produce a variety of possible effects: color, motion, light, smoke, noise, or other manners of "work."

The desired pyrotechnic effect must be carefully considered when a fuel is selected to pair with an oxidizer for a high-energy mixture. Both the flame temperature that will be produced and the nature of the reaction products are important factors. As some examples to highlight this point, the requirements and considerations for some of the major pyrotechnic categories are as follows:

1. *Propellants*: A combination producing high reaction temperature, a large volume of low molecular weight gas, and a rapid burning rate is needed. The rapid generation of gas, which quickly expands in one direction will "push" the vehicle that is to be propelled in the other direction.[4] Charcoal and organic compounds, such as polybutadiene, are often found in these compositions because of the gaseous products formed upon their combustion. An energetic metal fuel, such as aluminum, can be added to speed up the burning rate by a combination of enhanced heat output and enhanced thermal conductivity for the burning material to aid in propagation. However, metal fuels will not enhance *gas* production in propellants, since their combustion products are largely solid metal oxides and not the requisite gas.
2. *Illuminating compositions*: A high reaction temperature is mandatory to achieve intense light emission, along with the presence in the flame of strong light-emitting species (often measured in lumens or candle power). Magnesium is commonly found in such mixtures due to its good heat output and high flame temperatures. The production of incandescent magnesium oxide particles in the flame aids in achieving good light intensity. Atomic

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[4] Recalling Newton's third law "for every action there is an equal and opposite reaction."

sodium, present in vapor form in a flame, is a very strong light emitter, and sodium emission dominates the light output from the widely used sodium nitrate–magnesium compositions. Some common alternatives to magnesium are aluminum, "magnalium" alloy of magnesium and aluminum, and tungsten (explored further in Chapter 10)

3. *Colored-flame compositions*: A high reaction temperature produces maximum light intensity but color quality depends upon the proper emitters being present in the flame, with a minimum of solid and liquid particles present that are emitting a broad spectrum of "white" light that can wash out the desired color. Magnesium is sometimes added to colored-flame mixtures to obtain higher intensity, but the color quality may suffer due to broad emission from MgO particles. Organic fuels (such as red gum and dextrine) are found in most color mixtures used in the fireworks industry, with magnalium (magnesium–aluminum alloy) now widely added to color compositions to raise flame temperature, color brightness, and heat output.
4. *Colored-smoke compositions*: The creation of colored smokes requires a solid-colored organic dye in the composition to be scattered into the air. Gas evolution is needed to help disperse the colored-smoke particles. High temperatures are not desirable here because decomposition of the complex organic dye molecules will occur, denaturing the molecule from having the desired color. Metals are not found in these mixtures. Low-energy fuels such as sulfur and sugars are commonly employed.
5. *Ignition compositions*: Hot solid or liquid particles are desirable in igniter and first-fire compositions to insure the transfer of sufficient heat to ignite the intended main composition. Fuels producing mainly gaseous products are not commonly used. Fuels such as boron and zirconium that produce good heat output and lots of hot particulate reaction products are often used.

A good fuel will react with oxygen (or a halogen-like fluorine or chlorine) to form a stable compound, and substantial heat will be evolved. The considerable strength, and energetic formation, of the metal-oxygen (or metal-halogen) bonds in the reaction products accounts for the excellent fuel properties of many of the metallic elements. However, if high heat output is not desired, as discussed, less energetic fuels such as sugar (an organic) or sulfur (inorganic) might be used.

A variety of materials can be used as fuels in energetic mixtures, and the choice of material will depend on a variety of factors, with major considerations:

1. the amount of heat output required
2. the difficulty of ignitibility desired
3. the rate of heat release needed
4. the cost of the materials
5. the stability of the fuel and fuel–oxidizer pair
6. the amount of gaseous product desired.

Fuels can be divided into three main categories: metals, non-metallic/elements, and organic compounds.

INTRODUCTION TO METAL FUELS

A good metallic fuel resists air oxidation and moisture, has a high heat output per gram, and is obtainable at moderate cost in a range of particle sizes including very fine materials and coarser particles as needed. Both aluminum and magnesium, as well as the alloy "magnalium" of these two metals, are the most widely used materials. Titanium, zirconium, iron, manganese, copper, zinc, tungsten, and other metals are also used in various applications.

The alkali and alkaline earth metals—such as sodium, potassium, barium, and calcium—would make excellent high-energy fuels, but, except for magnesium, they are too reactive with moisture and atmospheric oxygen. Sodium metal, for example, reacts violently with water and must be stored in an inert organic liquid, such as xylene, to minimize its oxidation. One row down on the periodic table, potassium metal reacts even more violently than sodium.

A metal can initially be screened for pyrotechnic possibilities by an examination of its standard reduction potential (Table 2.5). A readily oxidizable material will have a large, negative value, meaning it possesses little tendency to *gain* electrons and a significant tendency to *lose* them. Good metallic fuels will also be reasonably lightweight, producing high calories/gram values when oxidized. Table 3.4 lists some of the common metallic fuels and their properties.

Recent developments in the area of metallic fuels, such as aluminum, have largely focused on interest in "nanopowders". While particles in the 1 μm range (1 μm, 1×10^{-6} m) have traditionally been considered "fine," these new powders have particle sizes in the 10^{-8} to 10^{-9} m range. These ultrafine powders exhibit the expected enhanced reactivity, but also pose some stability concerns—such as the possibility of being pyrophoric—with respect to oxidation due to their large surface area per gram (Brousseau and Anderson 2002; Jones and et al. 2003). Indeed, that large surface area per gram can mean poor long-term stability in air: The surface of these tiny particles will be oxidized to Al_2O_3, no longer a fuel, with little extra metallic aluminum left over inside the oxidized outer layer to act as a useful fuel! These nanopowders would have to be stored air-tight and used quickly upon mixing into a pyrotechnic composition, but in some applications, the extra effort for the effect could be worthwhile.

Metals also have the notable properties of being electrically and thermally conductive, that is, will take on and transfer electrons/electricity and heat throughout their mass to anything connected to it. Electrical conductivity can be a benefit for desired ignition via spark, as well as a serious hazard for *undesired* ignition! Thermal conductivity can aid in the propagation of a reaction by transferring excess heat from the pyrotechnic flame through the unreacted material (sometimes referred to as "preheating the zone"), speeding up the overall process. These effects are explored further in Chapters 6 and 7. Organic fuels and non-metallic inorganic fuels do not present these effects as substantially.

Let us explore some of the more common metallic fuels:

TABLE 3.4
Properties of Metallic Fuels

Element	Symbol	Atomic Weight	Melting Point, °C[a]	Boiling Point, °C[a]	Heat of Combustion, kcal/g[b]	Combustion Product	Grams of Fuel Consumed per Gram of O
Aluminum	Al	27.0	660	2,467	7.4	Al_2O_3	1.12
Copper	Cu	63.5	1,085	2,562	–	Cu_2O/CuO	7.94/3.97
Iron	Fe	55.8	1,535	2,750	1.8	Fe_2O_3	2.32
Magnesium	Mg	24.3	649	1,107	5.9	MgO	1.52
“Magnalium”	Mg/Al (~50/50 alloy)	–	460	–	–	MgO/Al_2O_3	1.32
Titanium	Ti	47.9	1,660	3,287	4.7	TiO_2	1.50
Tungsten	W	183.8	3,410	5,660	1.1	WO_3	3.83
Zinc	Zn	65.4	420	907	1.3	ZnO	4.09
Zirconium	Zr	91.2	1,852	4,377	2.9	ZrO_2	2.85

[a] Weast (1994).

[b] Shidlovskiy (1964).

ALUMINUM (Al)

The most widely used metallic fuel is probably aluminum, with magnesium running a close second. Aluminum is reasonable in cost, lightweight, stable in storage, available in a variety of particle shapes and sizes, and can be used to achieve a variety of effects (Kosanke and Kosanke 1993).

Aluminum has a melting point of 660°C and a boiling point of approximately 2,500°C. Its heat of combustion is 7.4 kcal/g. Aluminum is available in either "flake" or "atomized" form. The "atomized" variety consists of spheroidal particles. Spheres yield the minimum surface area (and hence minimum reactivity) for a given particle size, but this form will be the most *reproducible* in performance from batch to batch. Atomized aluminum, rather than the more reactive flake material, is used by the military for heat and light-producing compositions because the variation in performance from shipment to shipment is usually less.

Large flakes, called "flitter" aluminum, are widely used by the fireworks industry to produce bright white sparks. Aluminum in fine flake form can be quite reactive with a range of oxidizers. A special "pyro" grade of aluminum is also available from some suppliers. This is a dark gray powder consisting of small particle sizes (less than 50 μm) and high surface area, and it is *extremely* reactive. The smaller the particle size of the flake aluminum, the more sensitive and reactive it will be. Fine flake aluminum is used to produce explosive mixtures for fireworks, and combinations of oxidizers with this "pyro" aluminum should only be prepared by skilled personnel, and only made in small batches. Their explosive power can be substantial, and they can be quite sensitive to ignition by spark and flame.

Aluminum surfaces are readily oxidized by the oxygen in air, and a tight surface coating of aluminum oxide (Al_2O_3) is formed. While disadvantageous as a fuel, the white oxide coating protects the inner metal from further oxidation. Hence, aluminum powder can be stored for extended periods with little continuing loss of reactivity due to air oxidation (noting that the reactivity of relatively fresh aluminum may be greater than aluminum that has developed an oxide coating). Some manufacturers will prepare their aluminum powders with a coating of carbon/graphite (German Blackhead) or coated with Teflon® to protect against the oxide coating forming, preserving reactivity.

Metals that form a loose oxide coating on exposure to air—such as magnesium or iron—are not provided this surface protection, and extensive decomposition can occur during storage unless appropriate precautions are taken.

Compositions made with aluminum tend to be quite stable. However, moisture must be excluded if the mixture also contains a nitrate oxidizer. Otherwise, a reaction of the type

$$3KNO_3 + 8Al + 12H_2O \rightarrow 3KAlO_2 + 5Al(OH)_3 + 3NH_3 \tag{3.18}$$

can occur, evolving heat and ammonia gas. This reaction is catalyzed and accelerated by the alkaline medium generated as the reaction proceeds, and autoignition is possible in a confined situation. A small quantity of a solid weak acid such as boric acid (H_3BO_3) can effectively retard this decomposition by neutralizing the alkaline products and maintaining a weakly acidic environment. The hygroscopicity of the oxidizer is also important in this decomposition process. Sodium nitrate and aluminum cannot be used together, due to the high moisture affinity of $NaNO_3$, unless the aluminum powder is coated with a protective layer of wax or similar material. Alternatively, the product can be sealed in a moisture-proof packaging to exclude the presence of any water following the manufacturing process (Shidlovskiy 1964). Potassium nitrate–aluminum compositions must be kept quite dry in storage to avoid decomposition problems, but mixtures of aluminum and non-hygroscopic barium nitrate can be stored with a minimum of precautions, as long as the composition does not actually get wet. However, mixtures of magnesium metal with nitrate salts do not have this alkaline-catalyzed decomposition problem. A magnesium hydroxide, $Mg(OH)_2$, coating on the metal surface apparently protects it from further reaction. This protection is not provided to aluminum metal by the alkaline-soluble aluminum hydroxide, $Al(OH)_3$.

MAGNESIUM (Mg)

Magnesium is a very reactive and widely available metal that makes an excellent fuel under the proper conditions. It is oxidized by moist air to form magnesium hydroxide, $Mg(OH)_2$, and it readily reacts with all acids, including weak species such as vinegar (5% acetic acid) and boric acid. The reactions of magnesium with water and an acid (HX) are shown as follows:

$$\text{Water: } Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 \tag{3.19}$$

$$\text{Acids}(HX)\text{: } Mg + 2HX \rightarrow MgX_2 + H_2 (X = Cl, NO_3, \text{etc.}) \tag{3.20}$$

Even the ammonium ion, NH_4^+, is acidic enough to react with magnesium metal. Therefore, ammonium perchlorate and other ammonium salts should not be used with magnesium unless the metal surface is coated with linseed oil, paraffin oil, or a similar material.

Chlorate and perchlorate salts, in the presence of moisture, will also oxidize magnesium metal, destroying the pyrotechnic effect during storage. Nitrate salts appear to be considerably more stable with magnesium (Shimizu, Fireworks—*The Art, Science and Technique* 1981). Again, coating the metal with an organic material, such as paraffin, will increase the storage lifetime of the composition. A coating of potassium dichromate on the surface of the magnesium has also been recommended to aid in stability (Shimizu, Fireworks—*The Art, Science and Technique* 1981), but the toxicity of this material makes it of questionable value for industrial applications.

Magnesium has a heat of combustion of 5.9 kcal/g, a melting point of 649°C, and a relatively low boiling point of 1,107°C as compared to other metals. This low boiling point allows excess magnesium in a mixture to vaporize and burn with ambient oxygen in the air in the pyrotechnic flame, providing additional heat (and light) in flare compositions. In this effect, no extra heat absorption is required to decompose an oxidizer to react with the magnesium since the excess magnesium reacts with atmospheric oxygen; hence, the extra heat gained by incorporating the excess magnesium into the mixture can be substantial.

Magnesium metal is also capable of reacting with other metal ions in an electron-transfer reaction, such as

$$Cu^{2+} + Mg \rightarrow Cu + Mg^{2+} \tag{3.21}$$

This process becomes much more probable if a composition is moistened, again pointing out the variety of problems that can be created if water is added to a magnesium-containing mixture. The standard potential for the Cu^{2+}/Mg system is +2.72 V, indicating a very spontaneous process. Therefore, Cu^{2+}, Pb^{2+}, and other readily reducible metal ions must not be used in magnesium-containing compositions.

RECOVERY OF DEMILITARIZED MAGNESIUM: "GREEN" PYROTECHNICS RECYCLING

As we have seen, magnesium is a relatively abundant and useful pyrotechnic fuel. However, in certain legacy military compositions, a magnesium-based illuminant/flare containing sodium nitrate and a binder became "unserviceable," and a process was developed to recover the magnesium to be re-used in new compositions (J. Sabatini, et al. 2013). The munitions were taken apart kinetically and a water extraction was used to remove the sodium nitrate and binder, leaving crude magnesium which was further washed and purified before re-mixing into new compositions. The performance requirements for the magnesium, crucial for military use, were proved through experimentation and determining light output versus "virgin" compositions. In this way, modern green practices of "reuse and recycle" have found their way into pyrotechnic chemistry.

"MAGNALIUM" (MAGNESIUM–ALUMINUM ALLOY)

A material that has found significant popularity in pyrotechnics over the past 35 years is the 50/50 alloy of magnesium and aluminum, termed "magnalium," with a formula of Al_2Mg_3 and a melting point of 460°C (Shimizu, Fireworks—*The Art, Science and Technique* 1981). The alloy is considerably more stable than aluminum metal when combined with nitrate salts and reacts much more slowly than magnesium metal with weak acids. It offers some stability advantages of each metal with fewer of the stability disadvantages of each individually.

The Chinese pioneered wide use of magnalium in firework items to produce attractive white sparks, "crackling" effects, and bright color compositions. Shimizu also reports that a branching spark effect can be produced using magnalium with a black powder-type composition (Shimizu, Fireworks—*The Art, Science and Technique* 1981). Magnalium is now used widely around the world in the manufacturing of entertainment pyrotechnics, and we will see its use in numerous formulations in subsequent chapters.

IRON (Fe)

Iron, in the form of fine filings, will burn and incandesce and can be used to produce attractive orange-gold sparks, such as in the traditional wire handheld "sparkler." The small percentage (less than 1%) of carbon in steel can cause an attractive branching of the sparks due to carbon dioxide gas formation as the metal particles burn in air, "ejecting" the iron to burn like a small shooting star.

Iron filings are quite unstable on storage, however. They readily convert to iron(III) oxide (rust—Fe_2O_3) in moist air, and filings are usually coated with a paraffin-type material prior to use in a pyrotechnic mixture to protect against this. The loose iron oxide coating does not provide protection for the inner surface in the same manner that aluminum oxide coating does for aluminum particles.

Iron can produce a decent heat output when combined with a strong oxidizer such as potassium perchlorate. A composition consisting of iron and $KClO_4$ has been used in a variety of devices, including thermal batteries, when a mild heat source is required. The primary reaction that occurs should be

$$3KClO_4 + 8Fe \rightarrow 3KCl + 4Fe_2O_3 \tag{3.22}$$

which is stoichiometric at 48 parts $KClO_4$ and 52 parts iron by weight

OTHER METALS

Titanium metal (Ti) offers some attractive properties to the high-energy chemist. It is quite stable in the presence of moisture and most chemicals and produces brilliant silver-white spark and light effects with oxidizers. It is also possible to add titanium particles to color compositions and achieve an attractive effect of both color flame and white sparks. Lancaster feels that titanium is a safer material to use than magnesium or aluminum and recommends that it be used in place of iron filings in fireworks "fountain" items, due to its greater stability (Lancaster 1972). Cost seems to be the major factor keeping titanium from being a much more widely used fuel.

Zirconium (Zr) is another reactive metal, but its extreme spark-sensitivity (including discharge from common static electricity) is a major problem restricting its wider use in high-energy compositions. Zirconium in combination with potassium perchlorate ("ZPP" composition) is being used as an igniter material in electrically fired systems, and zirconium with iron(III) oxide is used in the military "A1A" ignition composition. Flame temperatures of oxidizer–zirconium compositions typically exceed 4,000°C. If you want a *really* hot pyrotechnic composition—to light another energetic material *very* quickly—zirconium is the fuel of choice.

The spark sensitivity of fine zirconium by itself—without any oxidizer present—is usually less than 1 mJ of spark energy. It is estimated that human-to-human static electricity shock (such as after rubbing one's feet on the carpet) can be around 15 mJ of energy; this is well more than enough energy to ignite zirconium, again putting zirconium compositions in a class by themselves. It makes no difference if the oxidizer is iron(III) oxide or potassium perchlorate, the resulting composition with zirconium will be *very* spark-sensitive. Therefore, zirconium is usually shipped wet, blended wet with oxidizer, and is finally allowed to dry when the composition has been incorporated in small amounts on bridgewires for electrical ignition or in other similar systems.

In summary, zirconium–oxidizer mixtures will be very sensitive to spark, and they will react very quickly to produce very high-temperature sparks ideal for ignition compositions. When you need to light something very quickly with high reliability, these might be materials you would choose. Otherwise, the sensitivity hazards of zirconium preclude wider use of the material.

Copper (Cu) is a less common fuel due to its cost but has found some use in colored-flame compositions when combined some chlorine donor, such as perchlorate oxidizers. Copper has a melting point of 1,085°C and a boiling point of 2,562°C. Copper is an excellent conductor of electricity and heat. Copper will oxidize to both copper(I) “cuprous” oxide (Cu_2O) and copper(II) “cupric” oxide (CuO) in pyrotechnic compositions depending on the flame temperature and other factors.

Tungsten (W, also classically referred to “wolfram” before standardized internationally), one of the heavier metals for the pyrotechnician, can be found in some delay compositions, but the cost often precludes widespread use. It has one of the highest melting points of any metal (3,410°C) and often needs a more energetic oxidizer, such as potassium perchlorate and/or barium chromate, to aid in propagation.

Zinc (Zn) is notable for its use in white smoke compositions. Zinc has a melting point of only 420°C, boiling at 907°C, so activation of this metal for oxidation and burning is relatively easy. Unreacted zinc can be prone to flash-boiling and burning in the air. Interestingly, zinc–sulfur compositions are used as a solid propellant as well as for the generation of white smoke since zinc sulfide will form—sulfur as an oxidizer and not a fuel—with the resulting interaction of the sulfide with moisture in the air showing as white smoke. The burning of zinc–sulfur compositions displays a very characteristic aquamarine-blue flame.

Recently, ytterbium (Yb)—a rare-early lanthanide—has been investigated for pyrotechnic usefulness (Koch, et al. 2012). Ytterbium has a slightly higher melting point than magnesium (824°C, vice 649°C) but a similar boiling point. Ytterbium burns with a luminous green flame, which could afford a replacement for barium-based green flame compositions. However, the cost of ytterbium is generally prohibitive for the everyday pyrotechnician and commercial fireworks, with small volume uses (such as military tracers) being one possible use.

INTRODUCTION TO NON-METALLIC/ELEMENTAL FUELS

Several readily oxidized nonmetallic elements have found widespread use in the field of pyrotechnics. The requirements again are stability to air and moisture, good heat-per-gram output, and reasonable cost. Materials in common use include sulfur, boron, silicon, and phosphorus. Their properties are summarized in Table 3.5.

SULFUR

The use of sulfur as a fuel in pyrotechnic compositions dates back to over 1,000 years, and the material remains a widely used component today in black powder, colored-smoke

TABLE 3.5

Properties of the Non-Metallic Elements Used as Fuels in High-Energy Mixtures

Element	Symbol	Atomic Weight	Melting Point, °C[a]	Boiling Point, °C[a]	Heat of Combustion, kcal/g[b, c]	Combustion Product	Grams of Fuel Consumed per Gram of O
Boron	B	10.8	2,300	2,550	14.0	B_2O_3	0.45
Carbon (charcoal)	C	~12	Decomp.	–	7.8	CO_2	0.38
Phosphorous (red)	P	31.0	590	Sublimates	5.9	P_2O_5	0.78
Phosphorous (yellow)	P_4	124.0 (as P_4)	44	–	5.9	P_2O_5	0.78
Silicon	Si	28.1	1,410	2,355	7.4	SiO_2	0.88
Sulfur	S	32.1	119	445	2.2	SO_2	1.00

[a] Weast (1994).
[b] Shidlovskiy (1964).
[c] Shimizu (2004).

mixtures, and firework compositions. For pyrotechnic purposes, the material termed "flour of sulfur" that has been crystallized from molten sulfur is preferred due to its expected high purity. Sulfur purified by sublimation—termed "*flowers* of sulfur"—often contains significant amounts of oxidized, acidic impurities and can be quite hazardous in high-energy mixtures, especially those containing a chlorate oxidizer (Lancaster 1972).

Sulfur has a particularly low (119°C) melting point. It is a rather poor fuel in terms of heat output, but it frequently plays another very important role in pyrotechnic compositions. It can function as a "tinder" or a fire starter. Sulfur undergoes exothermic reactions at low temperature with a variety of oxidizers, and this heat output can be used to trigger other, higher energy reactions with better fuels. Sulfur's low melting point provides a liquid phase, at low temperature, to assist the ignition process. The presence of sulfur, even in small percentage, can dramatically affect the ignitibility and ignition temperature of high-energy mixtures. Sulfur, upon combustion, is converted to sulfur dioxide gas and to sulfate salts (such as potassium sulfate—K_2SO_4). Sulfur is also found to act as an oxidizer in some mixtures, winding up as the sulfide ion (S^{2-}) in species such as potassium sulfide (K_2S), a detectable component of black powder combustion residue, as well as winding up as zinc sulfide (ZnS) in zinc–sulfur compositions.

When present in large excess, sulfur may volatilize out of the burning mixture as a yellowish-white smoke. A 1:1 ratio of potassium nitrate and sulfur makes a respectable smoke composition employing this behavior.

BORON

Boron is a reasonably stable metalloid element, produces no gas upon oxidation, and can be oxidized to yield good heat output. Boron is used in green flame compositions as alternative to compositions with barium-based oxidizers. The low atomic weight of boron (10.8) makes it an excellent fuel on a calories/gram basis. Boron has a high melting point (2,300°C), and it can prove hard to ignite when combined with a high-melting oxidizer. With low-melting oxidizers, such as potassium nitrate (a mixture referred to in the pyrotechnics industry as "$BKNO_3$"), boron ignites more readily yielding good heat production (and, if confined, can deflagrate with some energy). The low melting point of the oxide product (B_2O_3) can interfere with the attainment of high reaction temperatures, however, as the boron oxide will pull excess heat for melting that would otherwise be used to heat the system (Shidlovskiy 1964).

Boron is a relatively expensive fuel, but it frequently proves acceptable for use on a cost basis because only a small percentage is required (remember, it has a low atomic weight). For example, the reaction

$$\mathrm{BaCrO_4 + B \rightarrow various\ products\left(B_2O_3, BaO, Cr_2O_3\right)}$$

burns well with only 5% by weight boron in the composition (Ellern 1968). Boron has been virtually unknown in the fireworks industry (often banned by law in consumer fireworks), but it is a widely used fuel in igniter and delay composition for military and aerospace applications, as well as a potential replacement for barium compounds for green light/flame production. Boron with barium chromate or red iron oxide are known as useful delay systems.

Titanium–boron compositions are essentially gasless "solid state" reactions that, while difficult to ignite unless at high temperatures, are highly exothermic and a useful heat-generating mixture with TiB_2 as the product (Burke and et al. 1988). The reactants are also generally stable at normal ambient conditions, relatively insensitive to ignition as compared to other systems, and no special handling is required, making it a useful system if needed.

If there is a negative associated with boron, it is its tendency to readily undergo air oxidation, especially in the presence of moisture. This problem is aggravated by the significant weight gain that occurs when boron undergoes oxidation. In the reaction

$$2B + 3/2\,O_2 \rightarrow B_2O_3 \tag{3.23}$$

it can be calculated that 21.6 g (2 mol) of boron will convert to 69.6 g of boron oxide—a tripling of the weight. Hence the oxidation of a small percentage of the boron in a container awaiting measurement for addition to a mixer will cause the actual weight of boron being added to the mixture to be significantly less than the intended value. In a boron sample that has undergone 5% oxidation, the actual weight of elemental boron remaining in 10 g of the material has been reduced to 8.55 g—the remainder is boron oxide. This will cause a significant change in the performance of a pyrotechnic composition prepared from the oxidized boron. The solution is to wash boron with water (boron oxide is water soluble) prior to use, dry it in a low humidity environment, and store it in a tightly sealed container until it is weighed out.

Boron can also be found in two solid forms: "amorphous" boron (i.e., where the atoms making up a solid particle lack any specific order) and "crystalline" boron (where the atoms making up a solid particle are organized in a long-range order). Amorphous boron is the variant that has most often been used in pyrotechnics due to its availability and decreased expense versus crystalline boron though some work has shown that crystalline boron can prolong burn rates in green flame compounds in addition to providing some chemical resistance to long-term oxidation shown in Equation 3.23 (Sabatini, Poret, and Broad, Use of Crystalline Boron as a Burn Rate Retardant toward the Development of Green-Colored Handheld Signal Formulations 2011).

SILICON

In many ways similar to boron, silicon is a safe, relatively inexpensive fuel used in igniter and delay compositions. Silicon is a "metalloid" or semi-metallic element, meaning it has properties of metals as well as properties of non-metals. It has a high melting point (1,410°C), and combinations of this material with a high-melting oxidizer may be difficult to ignite. The oxidation product, silicon dioxide (SiO_2), is high melting and, importantly, is environmentally acceptable. Silicon has been used for a number of years, with red lead oxide (Pb_3O_4) as the oxidizer, to produce fast-burning delay mixtures for use in blasting caps. The delay columns are manufactured with a range of delay times and each provides a brief time lag (measured in milliseconds) between the firing signal and detonation of the cap. This allows the explosives engineer to design a blasting pattern whereby all of the explosive charges that have been carefully and systematically placed in a quarry or mine do not detonate simultaneously. The resulting brief delays produce a blast pattern that can aid greatly in reducing fly rock and ground vibrations compared to a blast where all charges are detonated simultaneously.

The reaction of silicon with iron oxide is an example of a moderate reactivity, low gas formulation seeking an application. The reaction zone moves through the composition as an incandescent zone, with minimum flaming. The reaction products (iron and silicon dioxide) are environmentally acceptable by most current criteria. The reaction is

$$2Fe_2O_3 + 3Si \rightarrow 4Fe + 3SiO_2 \tag{3.24}$$

which is stoichiometric at 83% iron(III) oxide and 17% silicon.

PHOSPHORUS

Phosphorus is an example of a material that is too reactive to be of any general use as a pyrotechnic fuel although it is employed in military white smoke compositions, and it has traditionally been used in toy pistol caps and trick noise makers (party poppers) to produce an audible report (Koch 2005).

Phosphorus is available in two forms, white (or yellow) and red. White phosphorus appears to be molecular, with a formula of P_4. It is a waxy solid with a melting point of 44°C and ignites spontaneously on exposure to air. It must be kept cool and is usually stored under water. It is highly toxic in both the solid and vapor form and causes burns on contact with the skin. Its use in pyrotechnics is limited to incendiary and white smoke compositions. The white smoke consists of the combustion product combined with atmospheric moisture and is primarily phosphoric acid (H_3PO_4).

Red phosphorus—an amorphous linkage of phosphorus atoms—is somewhat more stable and is a reddish-brown powder with a melting point of approximately 590°C (in the absence of air). In the presence of air, red phosphorus ignites near 260°C (Shimizu, Fireworks—*The Art, Science and Technique* 1981). Red phosphorus is insoluble in water. It is easily ignited by spark or friction and is quite hazardous any time it is mixed with oxidizers or flammable materials. Its fumes are highly toxic (Military Pyrotechnic Series Part Three: "Properties of Materials Used in Pyrotechnic Compositions" 1963).

Red phosphorus is mixed as a water slurry with potassium chlorate for use in toy caps and novelty noise makers such as "party poppers." These mixtures are quite sensitive to friction, impact, and heat and a large amount of such mixtures must never be allowed to dry out in bulk form. Red phosphorus is also used in white smoke mixtures, and several examples can be found in Chapter 11.

The sensitivity of "naked" red phosphorus to moisture and air, which will convert to phosphorus-based acids that can erode the container, can be mitigated by so-called "microencapsulation" of the material in a protective, hydrophobic substance. Studies showed that covering the red phosphorus particles in a phenolic resin (not unlike a wax or plastic material) increased the ignition temperature (i.e., less sensitive to heat), decreased hygroscopicity (i.e., less susceptible to moisture), and decreased friction sensitivity in a smoke composition (Liu and Guan 2017). For compositions where red phosphorus is useful, but the critical feature is *not* its sensitivity, this may be a viable solution for long-term storage of red phosphorus-based mixtures.

SULFIDE COMPOUNDS

Several metallic sulfide compounds have been used as fuels in pyrotechnic compositions. Antimony trisulfide, Sb_2S_3, is a reasonably low-melting material of 548°C, with a heat combustion of approximately 1 kcal/g. It is easily ignited and can be used to aid in the ignition of more difficult fuels, serving as a "tinder" in the same way that elemental sulfur does. It has been used in the fireworks industry for white fire compositions and has been used in place of sulfur in "flash and sound" mixtures with potassium perchlorate and aluminum.

Realgar (arsenic disulfide, As_2S_2) is an orange powder with a melting point of 308°C and a boiling point of 565°C (Shimizu, Fireworks—*The Art, Science and Technique* 1981). Due to its low boiling point, it has been used in yellow smoke compositions (in spite of its toxicity) and has also been used to aid in the ignition of difficult mixtures. The use of all arsenic compounds—including realgar—is prohibited in "common fireworks" (the type purchased by individuals) by regulations of the U.S. Consumer Product Safety Commission, arsenic being toxic to humans and animals (U.S. Consumer Product Safety Commission 2017).

INTRODUCTION TO ORGANIC FUELS

A variety of organic ("carbon-containing" in chemistry science) fuels are commonly employed in high-energy compositions. In addition to providing heat, these materials also generate significant gas pressure through the production of carbon dioxide (CO_2) and water vapor in the reaction zone.

The carbon atoms in these molecules are oxidized to carbon dioxide if sufficient oxygen is present. Carbon monoxide (CO) and elemental carbon are produced to varying amounts in an oxygen-deficient atmosphere, and a "sooty" flame is observed if a substantial amount of carbon is generated. The hydrogen present in organic compounds winds up usually as water molecules. For a fuel of formula $C_xH_yO_z$, x moles of CO_2 and $y/2$ moles of H_2O will be produced per mole of fuel that is burned. To completely combust this fuel, $x+y/2$ moles of oxygen gas ($2x+y$ moles of oxygen atoms) will be required. The amount of oxygen that must be provided by the oxidizer in a high-energy mixture is reduced by the presence of oxygen atoms in the fuel molecule. The balanced equation for the combustion of glucose, a sugar, is shown below:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \tag{3.25}$$

Only six oxygen molecules are required to oxidize one glucose molecule, due to the presence of six "internal" oxygen atoms in glucose. There are 18 oxygen atoms on both sides of the balanced equation.

A fuel that contains only carbon and hydrogen—termed a hydrocarbon—will require more moles of oxygen per gram for complete combustion than an equal weight of glucose or other oxygen-containing compounds. A greater weight of oxidizer is therefore required per gram of fuel when a hydrocarbon-type material is used.

The grams of oxygen needed to completely combust a given fuel can be calculated from the balanced chemical equation. Use the Pyro Valence method discussed in the previous chapter to determine the proper ratio of oxidizer to fuel for the stoichiometric composition. A sample calculation is shown as follows:

Potassium chlorate with glucose
Valence of $KClO_3 = -6$
Valence of glucose $= +24$
Mole Ratio is 1:4

Balanced equation:	$C_6H_{12}O_6$	+	$4KClO_3$	$\rightarrow 6CO_2 + 6H_2O + 4KCl$
Moles:	1		4	
Grams:	180		490	
Weight %	26.9		73.1	

For polymers, the repeat unit in the polymer chain is used for Pyro Valence calculations, using the formula weight of the repeat unit for mass calculations. For example, starch can be represented by $(C_6H_{10}O_5)_n$, with a formula mass per repeat unit of 162 and a Pyro Valence of +24 ($+24 + 10 - 10 = +24$). The Pyro Valence procedure discussed in the earlier chapter provides the easiest way to balance oxidizer/organic fuel systems, including those that contain polymers.

For example, assume that a fuel with molecular formula (or polymer repeat unit) of $C_{10}H_{12}O_2$ is to be used in a new pyrotechnic composition. First, we determine its Pyro Valence:

$$\underline{C} \qquad \underline{H} \qquad \underline{O}$$

$$\text{Pyro Valence} = 10(+4) + 12(+1) + 2(-2) = +48 \left(\underline{\text{very fuel rich}}\right)$$

To balance this material with an oxidizer, such as $KClO_4$, with a valence of −8 you will need $6KClO_4$s ($6 \times 8 = 48$) per mole of organic compound, or

$$6KClO_4 + C_{10}H_{12}O_2 \rightarrow 10CO_2 + 6H_2O + 6KCl$$

Balanced! It couldn't be any easier.

The more highly oxidized—or oxygen rich—a fuel is, the smaller its heat output *per gram* will be when it undergoes combustion (seen as a whole, the molecule is already partially oxidized). The flame temperature will also be lower for compositions using the highly oxidized fuel. Also, fuels that exist as hydrates (containing a water molecule or molecules as part of the solid crystal matrix) will evolve less heat than similar, non-hydrated species due to the absorption of heat required to vaporize the water present in the hydrates. It is also important to include the molecular weight of the water molecule (18 g/mol) in the calculation of the molecular weight of the hydrated fuel. A number of gums, resins, waxes, and similar natural products are available for use in energetic mixtures, and data on the base compositions and heats of formation for many of them has been published (Meyerriecks, Organic Fuels: Composition and Formation Enthalpy Part I—Wood Derivatives, Related Carbohydrates, Exudates, & Resins 1998; Meyerriecks, Organic Fuels: Composition and Formation Enthalpy Part II—Resins, Charcoal, Pitch, Gilsonite, & Waxes 1999).

NATURAL ORGANIC FUELS: SHELLAC AND RED GUM

Two "hot" organic fuels are shellac and red gum. Shellac, secreted by an Asian insect (the lac bug), contains a high percentage of trihydroxypalmitic acid—$CH_3(CH_2)_{11}(CHOH)_3COOH$. This molecule contains a low percentage of oxygen and produces a high heat/gram value (Shimizu, Fireworks—*The Art, Science and Technique* 1981). Shellac is also useful as a binder in pyrotechnic compositions (see below). Shellac is useful in colored-flame production because it will not burn as hot as metallic fuels, the latter of which can wash out the color with too much full-spectrum white. Furthermore, if the right proportion of oxidizer is used, it will not generate excess ash and the resulting unwanted black body radiation.

Red gum is a complex mixture obtained from an Australian "grass tree" exudate that is harvested on Kangaroo Island. Its approximate base formula is $C_6H_7O_2$ with a Pyro Valence of +27/111 g of material (Meyerriecks, Organic Fuels: Composition and Formation Enthalpy Part I—Wood Derivatives, Related Carbohydrates, Exudates, & Resins 1998). It has excellent fuel characteristics and a low melting point/decomposition temperature to aid in ignition and tends to give a very "white" flame when combined with an oxidizer—there is a minimum of orange color in the flame and a minimum of smoke is produced. Thus, it can be used in high-quality color compositions with minimal interfering effects, similar to shellac.

While shellac and red gum are both useful fuels, safe to work with, and relatively inexpensive organic fuels for hobbyist and commercial pyrotechnics, they rarely find use in military or large industrial applications. Since the supply of either is based on the activity of insects and growth of trees on a specific island, sourcing large amounts can prove difficult. Furthermore, changes in weather or climate can influence the approximate base formulas of both, essentially eliminating any true standardization to the formula or quality control that one might find with metallic fuels or industrially processed carbohydrates (glucose) or hydrocarbons (wax).

CHARCOAL

Charcoal is another organic fuel, and it has been employed in high-energy mixtures for over a 1,000 years due to its abundance and ease of production with even rudimentary technology. It is prepared by heating wood in an oxygen-depleted environment. Volatile decomposition products and moisture are driven off and a residue that is primarily carbon remains. There can be significant batch-to-batch variation between charcoals from the same wood source. Shimizu reports that a highly carbonized sample of charcoal showed a 91:3:6 ratio of C, H, and O atoms (Shimizu, Fireworks—*The Art, Science and Technique* 1981). A representative formula of $C_{16}H_{10}O_2$ has been published for charcoal, with a formula weight of 235 g/mol and a Pyro Valence of +72 (Meyerriecks, Organic Fuels: Composition and Formation Enthalpy Part II—Resins, Charcoal, Pitch, Gilsonite, & Waxes 1999).

The pyrotechnic behavior of charcoal may also vary greatly depending upon the type of wood used to prepare the material. The surface area and extent of conversion to carbon may vary widely from wood to wood and batch to batch, and each preparation must be checked for proper performance (Rose July 1980). Historically, willow and alder have been the woods preferred for the preparation of charcoal by United States black powder manufacturers. Grape vines, eucalyptus, and numerous other carbon-containing materials have also been used elsewhere around the world.

Charcoal is frequently the fuel of choice when high heat and gas output as well as a rapid burning rate are desired. The addition of a small amount of charcoal to a sluggish composition will usually accelerate the burning rate and facilitate ignition. Being largely carbon in composition, charcoal will have a high fuel/gram content, and a Pyro Valence value of +4/atomic weight of 12 can be used as an approximation in calculations if the actual carbon content of the charcoal is unknown.

Larger particles of charcoal in a pyrotechnic mixture will produce attractive orange sparks in the flame, a property that is often used to advantage by the fireworks industry. In this case, they are considered to be an added component that does not participate in the primary pyrotechnic reaction and are not included in oxygen-balance calculations.

CARBOHYDRATES

The carbohydrate family consists of a large number of naturally occurring oxygen-rich organic compounds. The simplest carbohydrates—sugars—have molecular formulas fitting the pattern $(C \bullet H_2O)_n$, and appeared to early chemists to be "hydrated carbon." The more complex members of the family deviate from this pattern slightly (Meyerriecks, Organic Fuels: Composition and Formation Enthalpy Part II—Resins, Charcoal, Pitch, Gilsonite, & Waxes 1999).

Examples of common sugars include glucose ($C_6H_{12}O_6$), lactose ($C_{12}H_{22}O_{11}$), and sucrose ($C_{12}H_{22}O_{11}$). Starch is a complex polymer composed of glucose units linked together. The molecular formula of starch is similar to $(C_6H_{10}O_5)_n$, and the molecular weight of starch is typically greater than 1 million. Reaction with acid breaks starch down into smaller units. Dextrine, a widely-used pyrotechnic fuel and binder, is partially hydrolyzed corn starch. Its molecular weight, solubility, and chemical behavior may vary considerably from supplier to supplier and from batch to batch. The testing of all new shipments of dextrine, as with most chemicals, is required for reproducibility and performance in pyrotechnic production.

The sugars also represent another example of the use of electronegativity and partial charges to explain reactivity. In the various sugar molecules, there are usually oxygen atoms bonded to a series of consecutive carbon atoms. This creates a chain of carbon atoms with adjacent partial positive charges and tends to result in low decomposition temperatures for compounds in the sugar family. Cooks are familiar with the tendency of sugars to caramelize at low temperature in a cooking pan. This "caramelization" is the result of bond-breaking and subsequent polymerization of the sugar to form tasty treats for the dessert table. In pyrotechnics, this bond breaking and the creation of reactive "free radicals" are responsible for the low ignition temperatures observed with many oxidizer–sugar compositions.

This is particularly true when potassium chlorate is the oxidizer. We have discussed previously the fact that potassium chlorate begins decomposing and evolving reactive oxygen at temperatures under 200°C. When combined with sugar that is also decomposing at low temperatures, we see ignition temperatures that are under 200°C for potassium chlorate/glucose and potassium chlorate/sucrose compositions (see Chapter 6). When a differential thermal analysis (DTA, discussed in Chapter 5) is run on such mixtures, an ignition exotherm is observed right as the melting point/caramelization temperature of the specific sugar is approached. Studies with other organic fuels have confirmed that it is the decomposition of the sugar molecules, rather than merely the solid–liquid phase change, that is responsible for the onset of ignition. Contrast this to higher melting metallic fuels, where it is often the decomposition of the oxidizer that is the foundation for the start of ignition.

The simpler sugars are used as fuels in various pyrotechnic mixtures. They tend to burn with colorless flame and give off less heat per gram than less-oxidized organic fuels. Lactose is used with potassium chlorate in some colored-smoke mixtures to produce a low-temperature reaction capable of volatilizing an organic dye with minimum decomposition of the complex dye molecules. It is also notable that since, in ideal burning situations, simpler sugars only give off carbon dioxide and water (and no solid oxide products as with metallic fuels), a stoichiometric combination with oxidizers that do not generate solid products—such as ammonium nitrate—will (again, ideally) generate *only* gaseous products as below with no solid residue:

$$C_6H_{12}O_6 + 12NH_4NO_3 \rightarrow 6CO_2 + 30H_2O + 12N_2 \qquad (3.26)$$

The simpler sugars can be obtained in high purity at moderate cost, making them attractive fuel choices given their burning temperatures. Toxicity problems tend to be minimal with these fuels, also. Concerns with sugars include their hygroscopicity, as well as the fact that some sugars occur as hydrates, with water as a component in the solid material.

More complex sugars, such as xanthan gum, are also used in pyrotechnic compositions. Xanthan gum is a "polysaccharide" generated by bacteria fermenting sucrose or glucose, and has a base chemical formula $C_{35}H_{49}O_{29}$. Xanthan gum is a food additive, so available widely, but has a known drawback of creating "slag" or a solid deposit that can retard proper burning.

OTHER ORGANIC FUELS

The number of possible organic fuels is enormous. Considerations in selecting a candidate are as follows:

1. *Extent of oxidation*: This will be a primary factor in the heat output per gram of the fuel.

2. *Melting point*: A low melting point, particularly when accompanied by a low decomposition temperature, can aid in ignitibility and reactivity. A melting point that is too low can cause production and storage problems. A good minimum value for a melting point might be 100°C.
3. *Boiling point/volatility*: If the fuel readily vaporizes or sublimes, the storage life of the mixture will be brief unless precautions are taken in packaging to prevent loss of the material.
4. *Chemical Stability*: An ideal fuel should be available commercially in a high state of purity and should maintain that high purity during storage. Materials that are easily air-oxidized, such as aldehydes, are usually poor fuel choices.
5. *Solubility*: Organic fuels frequently double as binders, and some solubility in water, acetone, or alcohol is required to obtain good binding behavior.
6. *Hydrate forms*: Some organic fuels exist as hydrates in their natural crystal forms, which can lower the performance in a pyrotechnic composition.

Materials that have been used in pyrotechnic mixtures include nitrocellulose (used in smokeless powder), polyvinyl alcohol, stearic acid, epoxy resins, and unsaturated polyester resins such as Laminac®. Salts of benzoic acid and its derivatives, such as potassium benzoate and sodium salicylate, also can serve as energetic fuels that are high-melting and quite stable. The properties of most of these fuels can be found in a handbook prepared by the U.S. Army (Military Pyrotechnic Series Part Three: *Properties of Materials Used in Pyrotechnic Compositions* 1963). Table 3.6 contains information on a variety of organic compounds that are of interest to the high-energy chemist.

Two other interesting organic, but non-oxygen containing, fuels are parlon and hexamethylenetetramine, or "hexamine." Parlon is a chlorinated rubber of base formula $C_6H_6Cl_2$ and is useful as a chlorine-donating fuel for color production—especially blue flame in the presence of copper oxide. Hexamine is another no-oxygen-containing organic fuel with formula $(CH_2)_6N_2$ and has been used in camping fuel tablets for many years (it is also the starting material for the synthetic high explosives RDX and HMTD). Hexamine is soluble in water, helpful for wet-mixing compositions, and is used in many colored-light "star" compositions.

BINDERS

An Overview of Binders

Many pyrotechnic compositions will often contain a small percentage (typically 2%–6% by weight) of an organic polymer that functions as a binder, holding all of the components together in a homogeneous blend that also provides mechanical strength to pressed or consolidated grains of composition. These binders, being organic compounds, will also serve as fuels in the mixture (see below) as well as generate gaseous and also possibly ashen, reaction products. Each binder, being a chemical and acting as a fuel, will have a heat of combustion, melting/decomposition temperature, gas volume/gram, sensitivity, and reactivity with other chemicals

TABLE 3.6
Properties of Some Common Organic Fuels

Compound	Formula	Molecular Weight	Melting Point, °C[a]	Grams of Fuel Consumed per Gram of O	Heat of Combustion, kcal/mol[b]
Monomers					
Glucose	$C_6H_{12}O_6$	180.2	146 (anhydrous)	0.94	670
Naphthalene	$C_{10}H_8$	128.2	80.5	0.33	1,232[a]
Shellac	Primarily $C_{16}H_{32}O_5$	ca. 304	ca. 120	ca. 0.44	–
Stearic acid	$C_{18}H_{38}O_2$	284.5	69.5	0.34	2,712
Sucrose	$C_{12}H_{22}O_{11}$	342.3	188 (decomposes)	0.89	1,351
Polymers					**cal/g[b]**
Dextrine	$(-C_6H_{10}O_5-)n\bullet H_2O$	–	Decomposes	ca. 0.94	ca. 4,179
Laminac	Polyester/styrene copolymer	–	ca. 200 (decomposes)	–	–
Nitrocellulose	$(C_6H_{10-x}O_{5-x}(ONO_2)_x)_n$	–	ca. 200 (decomposes)	–	2,409
Polyvinyl chloride	$(-CH_2CHCl-)_n$	ca. 250,000	ca. 80 (softens)	ca. 0.78	4,375
Starch	$(C_6H_{10}O_5)_n$	–	Decomposes	ca. 0.84	4,179

[a] Weast (1994).

[b] Military Pyrotechnic Series Part Three: “Properties of Materials Used in Pyrotechnic Compositions” (1963).

unique from the main fuel or fuels of the composition; even a small percentage of binder addition can affect the stability, ignitability, and overall performance of the composition. Analogously, *each different binder* will have a different heat of combustion, melting/decomposition temperature, gas volume/gram, sensitivity, and reactivity from other binders; therefore, different binders be simply swapped out on a pound-for-pound basis in a pyrotechnic formulation without the expectation that doing so might produce significant difference in exothermicity, burn rate, sensitivity to ignition stimuli, and gas output (Barisin and Batinic-Haberle 1994; Taylor and Jackson 1986; Barton and et al., The Influence of Binders in Pyrotechnic Reactions—Magnesium-Oxidant Systems 1984). Table 3.7 lists the fuel capacity of some common binders, and Table 3.8 lists the heats of combustion of some common binders.

Without the binder, component materials might well segregate during manufacture and storage due to variations in density and particle size (think of how small pebbles and sand will separate over time in a bucket). The "granulation process" —in which the oxidizer, fuel, and other components are blended with the binder (and usually a suitable solvent) and mechanically processed to produce grains of homogeneous composition of various sizes—is often a critical step in an overall manufacturing process for specific pyrotechnics (to include black powder for "muzzle loader" and other firearms). Solvent, if used, is evaporated following granulation, leaving a dry, homogeneous material. Alternatively, some liquid binders "cure"—toughen or harden—on exposure to air or by catalytic action, with a solvent not necessarily required for these systems. It is an important production factor that the solvent for the binder should not be capable of either reacting with or dissolving the oxidizer(s) or the main fuel(s). If one of the reactive components (oxidizer, primary fuel, other

TABLE 3.7
Fuel Capacity/Pyro Valence of Some Common Binders

Binder	Monomer Unit	Grams/ Unit	Pyro Valence/Unit	Pyro Valence/ Gram
Paraffin	C_2H_4	28	+12	+0.429
Polybutadiene	C_4H_6	54	+22	+0.407
Waxes	$\sim C_{36}H_{72}O_2$	536	+212	+0.396
Linseed oil	$\sim C_{17}H_{36}O_2$	272	+100	+0.368
Polyvinyl alcohol (PVA)	C_2H_4O	44	+10	+0.227
VAAR (vinyl alcohol-acetate resin)	$C_6H_{10}O_3$	130	+28	+0.215
Polyvinyl acetate	$C_4H_6O_2$	86	+18	+0.209
Laminac®	$\sim C_{20}H_{16}O_9$	400	+78	+0.195
Polyvinyl chloride (PVC)	C_2H_3Cl	62.5	+10	+0.160
Dextrine, starch, and gums	$C_6H_{10}O_5$	162	+24	+0.148
Viton®	$C_2H_2F_2$	64	+8	+0.125
Alloprene (Parlon®)	$C_{10}H_{11}Cl_7$	380	+44	+0.116
Nitrocellulose	$C_{12}H_{15}N_5O_{10}$	389	+43	+0.111 (12.5% N)
Teflon®	C_2F_4	100	−4 (→C)	−0.040

TABLE 3.8
Heats of Combustion and Oxidizer Consumption of Various Binders

Binder	Heat of Combustion (kcal/g)[a, b]	Weight of $KClO_4$ Consumed by 1 g of Binder	Weight of $PbCrO_4$ Consumed by 1 g of Binder
Paraffin	10.8	7.42	27.7
Polybutadiene	–	7.04	26.3
Waxes	10	6.85	25.5
Linseed oil	8.3	6.37	23.7
PVA	ca. 5	3.93	14.6
VAAR	ca. 5–6	3.72	13.9
Polyvinyl acetate	5.5	3.62	13.5
Laminac®	–	3.37	12.6
Polyvinyl chloride (PVC)	4.8	2.77	10.3
Dextrine/starch/gums	4.2	2.56	9.55
Viton®	–	2.16	8.06
Alloprene (Parlon®)	3.3	2.01	7.48
Nitrocellulose	2.6	1.92	7.16 (12.5% N)
Teflon®	–	0.692 ($\rightarrow CO_2$)	2.58

[a] Weast (1994).

[b] Barton and et al. (1984).

components) dissolves to a significant extent in the solvent, its original particle size will likely change when the solvent evaporates and the material is regenerated as a solid. This could cause variations in pyrotechnic performance. However, it some cases, it may be desirable to dissolve both the binder and fuel or oxidizer for more intimate mixing and if further post-processing can adjust the requisite particle size of the final composition.

In addition to aiding in achieving, and then maintaining, homogeneity in the composition, binders also reduce dusting in the manufacturing operations, permit control of bulk density through granulation, and—again, in an extremely important role—provide mechanical strength to compositions when they are pressed or formed into specific configurations by acting like a glue to hold the composition together. Some compositions are pressed into specific shapes, such as flat disks or long cylinders, and total performance can be affected, or even prevented from completion, if the shape is broken or crumbled. The binder will help maintain the composite shape.

For example: dextrine, or dextrin—which is produced from corn starch—has been widely used as a binder in the fireworks industry. Water is used as the wetting/activating agent for dextrin, avoiding the cost, environmental issues, and hazards associated with the use of organic solvents. Water-activated binders can only be used when the water does not react with one or more of the components of the mixture or produce particle size change in a component. *Thorough* drying will be required later in the manufacturing process to fully remove the water from the composition.

The U.S. military has used a material called VAAR (vinyl alcohol-acetate resin) as one of its primary binders for pyrotechnic compositions. VAAR is able to produce a good binding effect at low percentage by weight in many compositions compared to many of the other common binders. It is soluble in a methyl alcohol–methyl acetate solvent blend and displays excellent long-term stability with a variety of compositions (Military Pyrotechnic Series Part Three: *Properties of Materials Used in Pyrotechnic Compositions* 1963).

Other common binders include nitrocellulose (of lower than 12.6% nitrogen content, with acetone as the solvent), polyvinyl alcohol (used with water), and Laminac® (an unsaturated polyester crosslinked with styrene—the material is a liquid until cured by catalyst, heat, or both, and no solvent is required). Epoxy binders (the main chemical of which contains very reactive epoxide groups: a three-membered ring of two carbons and one oxygen that opens and bonds with anything suitable nearby) can also be used in liquid form during the mixing process and then allowed to cure to leave a final, rigid product. The caution with epoxy binders is the fact that many epoxy curing agents are amine (nitrogen) compounds, which are basic. One must be sure that the epoxy system is compatible with all other components in the composition.

In selecting a binder, the chemist seeks a material that will provide good homogeneity and performance with the minimal amount of binder possible. Organic materials will reduce the flame temperatures of compositions containing metallic fuels, and they can impart an orange color to flames if incomplete combustion of the binder occurs and carbon solids forms in the flame (recall black body radiation). A binder should be neutral and non-hygroscopic to avoid the problems that water and an acidic or a basic environment can introduce. For example, magnesium-containing mixtures require the use of a non-aqueous binder/solvent system, because of the reactivity of magnesium metal toward water. When iron is used in a composition, pretreatment of the metal with a wax or other protective coating is advisable, especially if an aqueous binding process is used, to avoid the oxidation of the iron to iron oxide (now an oxidizer, and possibly not a good one for the system).

MOST BINDERS ARE ALSO FUELS

Binders are critical components for energetic mixtures. In addition to their binding role, however, it is important to remember that most binders have fuel capability as well. At the 2%–5% level by weight, they can affect ignition temperature, burn rate, ignition sensitivity, gas output, water resistance, and hygroscopicity of a composition. Any change in binder—either the use of a new material or the use of a different percentage in a composition—requires a careful reevaluation of the properties of an energetic mixture, including sensitivity to ignition. Table 3.9, showing the effect of binder percentage a sodium nitrate/magnesium system, illustrates this point. The initial composition is 60 g $NaNO_3$ and 40 g Mg, and the table shows the

TABLE 3.9
Effect of Binder Percentage on the 60/40 Sodium Nitrate/Magnesium System

	Grams of Sodium Nitrate Consumable by Binder				
Additional Grams of Binder	**PB**	**PVA**	**VAAR**	**Gum**	**NC**
1	6.9	3.9	3.7	2.5	1.9
2	13.8	7.7	7.3	5.0	3.8
3	20.1	11.6	11.0	7.6	5.7
4	27.7	15.4	14.6	10.1	7.6
5	34.6	19.3	18.3	12.6	9.5
6	41.5	23.2	22.0	15.2	11.3
8	55.4	30.9	29.3	20.2	15.1
10	69.2	38.6	36.6	25.2	18.9

PB, polybutadiene; PVA, polyvinyl alcohol; VAAR, vinyl alcohol-acetate copolymer; Gum, starch or gum; NC, 12.5% nitrocellulose.

grams of $NaNO_3$ consumable by the binder acting as a fuel. A sample calculation is as follows:

$$NaNO_3 \text{Pyro valence/gram} = -5\text{P.V./mol}/85\,\text{g/mol} = -0.0588$$

$$\text{Polybutadiene(PB) Pyro valence/gram} = +22\text{P.V./unit}/54\,\text{g/unit} = +0.407 \text{for PB}$$

Therefore, the weight ratio for $NaNO_3$/PB will be 0.407/0.0588 = 6.9, to make the sum of the Pyro Valences = 0 (or produce a balanced or stoichiometric mixture of oxidizer and fuel-binder). One gram of PB (polybutadiene) will consume 6.9 g of sodium nitrate when the mixture is ignited. The conclusion drawn here is that the binder (or most organic compounds), present at even a relatively low level, can be a significant consumer of the available oxygen in a pyrotechnic mixture that might be intended for the main fuel.

RETARDANTS

Occasionally, a pyrotechnic mixture will function quite well and produce the desired effect, except for the fact that the burning rate is a bit too fast for the intended application. In this case, a change or addition is needed that will slow down the reaction without otherwise affecting performance, sensitivity, or storage stability. This can be accomplished by altering the ratio of ingredients (e.g., by reducing the amount of fuel) or by adding a component to the composition that is either inert or retards burning speed by reacting during the burning. Excess metallic fuel is less effective as a "coolant" because of the ability of many fuels—such as magnesium—to react with the oxygen in the air and liberate heat.[5] Also, metals tend to be excellent heat conductors, and an increase in the overall metal percentage by reducing the oxidizer content, intended to slow the reaction, can actually speed up a reaction by facilitating heat transfer through the composition during the burning process.

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[5] It goes without saying: excluding the oxygen in the air is exceptionally hard to do!

Materials that decompose at elevated temperatures with the absorption of heat (endothermic decomposition) can work well in some systems as rate retardants. Calcium and magnesium carbonate, and sodium bicarbonate, are sometimes added to a mixture for this purpose. Note the endothermic reactions:

$$\mathrm{CaCO_3(solid) + heat \rightarrow CaO(solid) + CO_2(gas)} \text{heat is absorbed} \tag{3.27}$$

$$\begin{aligned}\mathrm{2NaHCO_3(solid) + heat \rightarrow Na_2O(solid) + H_2O(gas)} \\ \mathrm{+ 2CO_2(gas)} \text{heat is absorbed}\end{aligned} \tag{3.28}$$

The gas generation that occurs may or may not affect the performance of the mixture by pre-heating unreacted components or separate unreacted components through propulsion effects; the solid formation that occurs can affect performance by creating ash that can emit orange or yellow light and leave undesired residue.

Although endothermic, these reactions are thermodynamically spontaneous at high temperature due to the favorable entropy change associated with the formation of random gaseous products from solid starting materials; in other words, two or more particles moving randomly is an increase in entropy over one particle and therefore are entropically favored.

In addition to chemicals that absorb heat by reacting with the pyrotechnic output, inert diluents, such as powdered clay and diatomaceous earth (which is mainly silicon dioxide, SiO_2), can also be used to retard burning rates. These materials both absorb heat (simply heating up) as well as separate the reactive components, thereby slowing the pyrotechnic reaction. The ignitability and sensitivity to ignition can also be affected by adding retardants such as these, however. Diatomaceous earth can coat otherwise free metallic magnalium, for example, leaving it protected from electrical/spark ignition and therefore less sensitive (if that is the primary ignition system). A stronger "jolt" of electricity will be needed in this case to break through the non-conductive inert material, depending on the amount of inert chemical used.

An example use of retardants would be the addition of magnesium carbonate or sodium bicarbonate to a mixture of potassium chlorate and sugar. Without the retarding "coolant," combustion of potassium chlorate and sugar can be quite rapid, and even deflagrating if confined. However, with the addition of the retardant, the mixture will burn in a more measured fashion and "cool." The pyrotechnician can "dial in" the intensity of the binary $KClO_3 + C_6H_{12}O_6$ composition by adding the retardant to the desired burn rate/intensity, even up to 50% by weight of $MgCO_3$ or $NaHCO_3$.

BRIEF NOTE ON COLORED DYES

One category of pyrotechnic components not discussed in depth in this chapter is "colored dyes" for colored-smoke compositions. Colored dyes can be present in significant quantities in colored-smoke pyrotechnic mixtures and, ideally, do not act as oxidizers or fuels or even decompose/react at all. Colored dyes could technically be thought of as a "retardant" as they will soak up heat to be vaporized into the air, followed by recondensation into intended "smoke." These dyes and colored-smoke production will be discussed in detail in Chapter 11.

CATALYSTS

Catalysts have been rarely used in pyrotechnic compositions over the years, the exception being considerable interest in the use of catalysts to accelerate the decomposition of oxidizers in propellant formulations. Catalysts work by providing an alternate reaction pathway of lower activation energy than the primary, uncatalyzed, pathway. Recall the reaction profile diagram from Figure 2.3 and imagine a new curve that doesn't need to go as "high," or take as much activation energy, to begin the downward slope. In energetic mixtures, the role of the catalyst is frequently to accelerate the decomposition of the oxidizer, often by providing a reactive surface site where the breakdown can occur. Decomposition of the oxidizer can be the initiating step in many pyrotechnic reactions, and quicker decomposition will lead to quicker reactions, which will be observed as a much more energetic overall effect.

It is usually possible to obtain the desired burn rate with a pyrotechnic mixture by the appropriate selection of components, varying their ratios, as well as by varying particle sizes of the components. However, interest in propellants has continued to focus on faster and faster burning materials (without instantaneous deflagration/detonation of course), and hence the interest in catalysts has become significant.

Ammonium perchlorate is the primary oxidizer used for solid rocket propellant formulations, in large part because of its gas-generating capabilities. Ammonium perchlorate has been shown to be capable of catalytic decomposition, with metal oxides, such as iron(III) oxide, the most commonly used materials. A low percentage of catalyst added to a propellant formulation can produce a significant increase in propellant burn rate.

Recent studies have looked mainly at transition-metal oxides (iron oxide, copper oxide) as well as "nano-metal" particles, so-called because their dimension is in the nanometer range (1 nm is one-billionth of a meter). Nano-metal particles have a much larger surface area in bulk and can therefore aid better in decomposition/burning of propellants by better surface interaction. Some interesting research into ferrocene—a molecule where an iron atom is sandwiched between two organic ring molecules—has also shown some promising results (Gao et al. 2011).

GAS VOLUME CONSIDERATIONS: A REVIEW

While discussed above as an addendum to various component and effect matters, a summary of gas volume considerations should be reiterated. The selection of an oxidizer and a fuel (and any additives such as binders, retardants, or catalysts) for a pyrotechnic or propellant composition, together with the weight ratio to be used, determines the heat output and the effects, *but also the gas output* for the mixture under consideration. It is possible to select components so that no significant gas is evolved or to select components to produce all gaseous products.

EXAMPLES

$$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3 \qquad \text{No gas products}$$

Iron(III) oxide and aluminum—a "thermite" reaction

$$2NH_4NO_3 + C \rightarrow 2N_2 + 4H_2O + CO_2 \qquad \text{All gas products}$$

Ammonium nitrate and carbon—a gas generator

In a similar manner that an oxidizer and fuel can be selected to yield high or low heat output per gram of composition, components are selected to yield high or low gas output per gram depending on what the system is desired to accomplish.

Production of gas can provide several effects, whether beneficial or detrimental to the desired effect. Hot gases can push through unreacted material, pre-heating along the way, and aid in increasing the burn rate. Hot gases can also be used to disperse reactants or products as appropriate. Hot gases are essential in smoke production but often undesired in colored flame if they obscure the light output. Sometimes, hot solid products, known as "slag," is the desired pyrotechnic effect, and gas production can hinder the condensed solidification of slag by getting in the way or breaking apart solid mass. Gas production will be discussed as it is advantageous, or disadvantageous, to various pyrotechnic phenomena as the specific systems are discussed in later chapters.

CONCLUSION AND BEST PRACTICES IN COMPONENT SELECTION

How many components should you use to produce an energetic mixture? Consider the idea that an "ideal" energetic material might be a one-component system: reduces or eliminates any variability in mixing, production, unwanted interactions, etc. The high explosive TNT is an example of this sort of "ideal" material: The pure compound is manufactured and then melted at its low melting point of 81°C and finally poured into containers to create explosive devices. Life could not be easier if all the chemist needs to do is blow things up! However, as we have seen, the universe of needs and possibilities with pyrotechnics goes far beyond the relatively straightforward destructive effect.

Therefore, with pyrotechnics and propellants, it is far more common to have to combine a group of chemicals to produce the effect, sensitivity, and burn rate one is seeking without being "ideal" in name. These compositions will include an oxidizer, a fuel, probably a binder, and additional components to fine-tune the composition and create the desired result. A good pyrotechnician will keep the number of components to a minimum for simplicity and avoiding unintended events. The probability of manufacturing problems arising over time (i.e., manufacturing the same composition and the same device every day and every month) goes up in what seems an exponential fashion as the number of components increases. Once one reaches even three or more components in a composition, reproducibility problems are almost certain to arise from time-to-time in production.

One must also take note of variations in the same chemical fuel/oxidizer/other from batch-to-batch, even from the same manufacturing company, that can affect overall performance. One batch of aluminum powder well-sealed from air exposure will act markedly different than one left out in the open to oxidize. One batch of potassium perchlorate manufactured and refined without good-quality practices may already be partially decomposed and not perform the same as one of near 100% purity. As previously noted, it should be stressed again that natural products (such as red gum or charcoal) can change from year-to-year based on weather, climate, sourcing, and of course manufacture/refining practices. When even a two-component composition is remade with a new batch or lot of chemical, the performance should always be double-checked to ensure no tweaking needs to be made.

Now that we have learned about the *chemicals* used in pyrotechnic compositions, we can use that knowledge to understand the *principles* of the how these chemicals interact and react in such compositions.

4 Pyrotechnic Principles

PURPLE STARS: Purple stars explode over water as gold mines fire underneath.

One major key to pyrotechnic reactivity is overall "homogeneity" of a composition, or uniform distribution of chemicals; anything one can do to make a composition more homogeneous should enhance its reactivity. But be careful, this may also enhance its sensitivity! Any action or change in pyrotechnic manufacture can sometimes lead to unforeseen outcomes: if you attempt to manufacture pyrotechnic articles, strange things will occur involving reactivity that seems to defy all logic. However, there is *always* some explanation for a change in pyrotechnic values—burn rate, sensitivity, candlepower, or other reactivity value—and the challenge is to identify the source of the variability. When things seem to be at their worst or most inexplicable, return to the basics of pyrotechnics in the search for an explanation, and, more importantly, a solution to the problem.

INTRODUCTION

The "secret" to maximizing the rate of reaction, and therefore burn rate, for a given pyrotechnic, propellant, or explosive composition can be revealed in a single word—homogeneity. *Ideal homogeneity* in a solid mixture would be the common proportional distribution and all particles throughout the mixture; that is, all particles are equally blended throughout with no areas of higher or lower concentration. Any operation that increases the thoroughness of the blending of a high-energy mixture should lead to an enhancement of reactivity. Reactivity, in general, refers to the rate—in grams- or centimeters-per-second (g/s or cm/s)—at which starting materials are converted into products. But, other performance factors—such as heat output, light output, or gas output—may be of equal or greater interest for a given situation.

The importance of "intimate mixing" was recognized as early as 1831 by Samuel Guthrie, Jr., a manufacturer of "fulminating powder" used to prime firearms.[1] Guthrie discovered that the performance of his mixture—a blend of potassium nitrate, potassium carbonate, and sulfur—could be dramatically improved if he first melted together the nitrate and carbonate salts and *then* blended in the sulfur. He wrote, "By the previously melting together of the nitro and carbonate of potash, a more intimate union of these substances was effected than could possibly be made by mechanical means" (Davis 1941).

However, he also experienced the hazards associated with maximizing reactivity, reporting, "I doubt whether, in the whole circle of experimental philosophy, many cases can be found involving dangers more appalling, or more difficult to be overcome, than melting fulminating powder and saving the product, and reducing the process to a business operation. I have had with it some eight or ten tremendous explosions, and in one of them I received, full in my face and eyes, the flame of a quarter of a pound of the composition, just as it had become thoroughly melted" (Davis 1941). An enormous debt is owed to these pioneers in high-energy chemistry who were not only willing to experiment (despite the obvious hazards and lack of personal protective equipment) but also report their potentially proprietary results so others could build on their knowledge.

Varying degrees of homogeneity can be achieved by altering either the extent of mixing or the particle size of the various components (or both, for maximum effect). Striking differences in reactivity can result from changes in either of these, as Mr. Guthrie observed with his "fulminating powder."

TECHNICAL PARAMETERS FOR PYROTECHNIC BEHAVIOR

A number of technical parameters related to burning behavior can be experimentally measured and used to report the "reactivity" or performance of a particular high-energy mixture and compared to other mixtures (Military Pyrotechnic Series Part One, "Theory and Application" 1967; Shidlovskiy 1964):

1. *Heat of Reaction*: This value is expressed in units of calories (or joules) per mole or calories (or joules) per gram and is determined using an instrument called a "calorimeter." One calorie of heat is required to raise the temperature of 1 gram of water by one degree on the Celsius scale[2]. The temperature rise of a measured quantity of water, brought about by the release of heat from a measured amount of high-energy composition, can be converted into calories

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[1] Scientifically, the "fulminate" ion is CNO^-, although the term had also been used colloquially to mean anything "explosive" since fulminate salts tend to be very unstable, sensitive to ignition, and quite energetic. Calling a product a "fulminating powder" would alert the consumer to the explosive nature of the material, even if no chemical fulminates were actually present.

[2] The "calories" labels seen on food packaging are actually *kilo*calories, or 1,000 standard calories.

of heat. Depending upon the intended application, a mixture liberating a high, medium, or low value may be desired. Some representative heats of reaction are given in Table 4.1. The experimentally measured heat of reaction can be compared to theoretical heats of reaction obtained from calculations using "heat of formation" values, as discussed in Chapter 1. It is always reassuring when experimental heats agree with the calculated values—this suggests that the expected reaction products are, in fact, forming over the course of the high-temperature reactions following ignition of the energetic material.

The actual atmosphere used for a "heat of reaction" experiment can play a critical role in determining the amount of heat that is produced and measured. If the ambient gas contains oxygen, reaction of fuels in the mixture may occur with the atmospheric gas—an oxidizer—present in the combustion chamber, in addition to the intended oxidizers present in the pyrotechnic composition.

TABLE 4.1
Representative Heats of Reaction for Pyrotechnic Systems

Composition	% by Weight	ΔH Reaction, kcal/g	Application
I. Magnesium	50	2.0	Illuminating flare
Sodium nitrate	44		
Laminac binder	6		
II. Potassium perchlorate	60	1.8	Photoflash
Aluminum	40		
III. Boron	25	1.6	Igniter
Potassium nitrate	75		
VAAR binder	+1%		
IV. Potassium nitrate	71	1.0	Starter
Charcoal	29		
V. Black powder	91	0.85	Flash and report
Aluminum	9		Military simulator
VI. Barium chromate	85	0.5	Delay
Boron	15		
VII. Silicon	25	0.28	First fire
Read lead oxide	50		
Titanium	25		
VIII. Tungsten	50	0.23	Delay
Barium chromate	40		
Potassium perchlorate	10		

The use of inert atmospheres, such as argon or helium gas, can prevent these fuel–atmospheric oxygen reactions from occurring. Experimenters must always be sure to report the atmosphere used in determining any heat output/calorimetric values, to include ambient temperature and pressure.

As a general "rule of thumb," a reaction that generates a heat of reaction of 1 kcal/g or greater is significantly exothermic, while a value exceeding 2 kcal/g is a very "hot" reaction. When a composition with a heat of reaction well below 1 kcal/g is encountered, concerns should begin to rise regarding the ability of the reaction to propagate under adverse conditions, such as low ambient temperatures, the presence of significant moisture, or the use of a small-diameter column of minimally confined energetic material.

2. *Burning rate*: This is typically measured in units of inches, centimeters, or grams per second for slow mixtures, such as delay compositions, and in meters per second for "fast" materials. Experimental results should always describe the physical state of the composition for mass-per-time reaction rates: loose powder, pressed into a tube, pressed into a pellet, etc., as these will all have different burn rates for the same material based on other factors. Furthermore, the length-per-time measurement (such as cm/s) must be clarified by explaining the confinement setup of the powder. For example, a composition pressed into a tube 0.5 cm wide will show a very different "cm/s" burn rate as compared to the same composition in a 1 cm wide tube.

   One way to alter burning rates is by varying the oxidizer or fuel that is used, as well as the ratios of ingredients, as shown in Table 4.2. Burning "rates" are also sometimes reported as "burn times," in units of s/cm or s/gram—the *inverse* of the previously stated units. Always carefully read the units when

TABLE 4.2
Burning Rates of Binary Mixtures of Nitrate Oxidizers with Magnesium Metal[b]

% Oxidizer (by Weight)	% Magnesium	Burning Rate (in./min)[a]	
		Barium Nitrate Oxidizer	**Potassium Nitrate Oxidizer**
80	20	2.9	2.3
70	30	–	4.7
68	32	5.1	–
60	40	10.7	–
58	42	–	8.5
50	50	16.8	13.3
40	60	38.1	21.8
30	70	40.3	29.3
20	80	"Erratic"	26.4

[a] Loading pressure was 10,000 psi into 1.4 in.^{2} cases.

[b] Military Pyrotechnic Series Part One, "Theory and Application" (1967).

examining burning rate data. When units of distance or mass per second are used, a larger value means a faster rate. When burn *time*s (seconds to burn 1 cm or 1 g of material) are used, the *smaller* number is the faster burning material.

The experimental burning rate depends on a number of variables that will be discussed in Chapter 6 of this book. To repeat, it is important to specify experimental conditions (such as ambient temperature/pressure/humidity, burn chamber pressure, loading or consolidation pressure) when reporting burn rates for energetic materials.

3. *Light intensity*: This is measured in units of candela or candlepower. The intensity is determined to a large extent by the temperature reached by the burning composition. Intensity from incandescent particles will increase exponentially (a 4th power relationship) as the flame temperature rises. We will explore this in depth in Chapter 10.
4. *Color quality*: This will be determined by the relative intensities of the various wavelengths of visible light emitted by vapor–phase species present in the pyrotechnic flame. Only those wavelengths falling in the visible region of the electromagnetic spectrum will contribute to the color. An *emission spectrum*, showing the intensity of light emitted at each wavelength over the wavelength range that is examined can be obtained if proper instrumentation—an emission spectrophotometer—is available. An example of this is shown in Figure 4.1. We will explore this in depth in Chapter 10.
5. *Volume of a gas produced*: Gaseous products are frequently desired as output when a high-energy mixture is ignited. Gas can be used to eject sparks, disperse smoke/dye particles, inflate a life-saving protective “airbag,” and provide propellant behavior. When severely confined, gas output can be used to create a “pressure-rupture” explosion. The presence of organic compounds—containing carbon, hydrogen, and perhaps nitrogen or sulfur—in an energetic material can generally be counted upon to produce significant amounts of gas products. Organic binders and sulfur should be avoided if a “gasless” or very low gas-producing, composition is desired. In addition, for a particular composition to be of practical interest as a gas generator, it must produce a significant amount of pyrotechnic effect *per gram* of mixture. Efficiency per unit *volume* is also an important consideration when available space is limited. Of course, gas volume is a function of temperature and pressure, as well as the number of moles of gas present (see the Ideal Gas Law in Chapter 2 of this book). When water is a significant product from an energetic material, the measured gas pressure (at constant volume) will decrease significantly from the initial pressure value as the products cool below 100°C, the condensation point of water.
6. *Pressure rate-of-rise*: Of the various measures of “performance” or “reactivity,” it is quite possible that the best method for comparing two batches or preparations of energetic material for reproducibility is the measurement of pressure generation versus time, following ignition of the material, sometimes referred to as the “United Nations Time/Pressure test” (United Nations 2015; ET Users Group 2016). This type of study—where a pyrotechnic is ignited in a closed vessel with a pressure transducer attached—provides

> the experimenter with both a time component and an output component, pressure-vs-time. Both the peak pressure and the time-to-reach peak pressure can directly correlate to the performance of the energetic material. Figure 4.2 shows an example time–pressure study on a potassium nitrate/sodium azide mixture (which had been used in car airbag systems).
>
> Based on best practices, if a batch of composition prepared on Monday and a batch prepared on Thursday give overlapping pressure rate-of-rise curves, the two batches should be expected to behave in a similar manner when they are loaded into end items in the manufacturing process. Understandably, gasless or low-gas compositions may not be suitable for this kind of technical measure.

It is crucial to remember: *there is no standard test fixture* for measurement of these technical parameters. The experimental setup, analytical equipment, atmospheric conditions, and overall method may all be different (not to mention differences between chemicals) from trial to trial. It is critical that the researcher understands the experimental conditions when reading results and comparing to their own work.

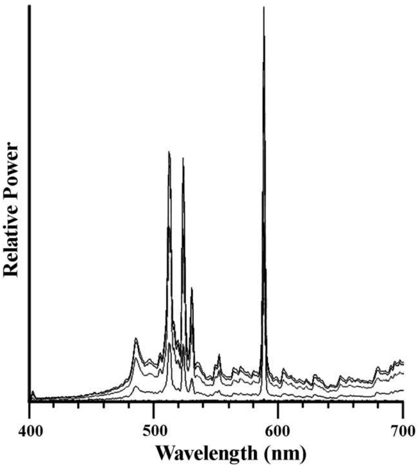

FIGURE 4.1 Light output "spectrum" from a green flare. The radiant output from a burning pyrotechnic composition can be analyzed using an instrument known as a spectrophotometer. Energy output can be monitored as a function of wavelength. A good "white light" mixture will emit reasonably intense light over the entire visible region. Color will be produced when the emission is concentrated in a narrow portion of the visible range. The output from this flare falls largely between 500 and 540 nm—the "green" portion of the human-eye-visible spectrum (the strong peak at approx. 589 nm is most likely from sodium impurities in the pyrotechnic mixture, further discussed in Chapter 10). Green light emission is usually associated with the presence of a barium compound in the mixture (which leads to the production of molecular BaCl in the vapor state upon ignition), typically the primary emitter of green light. Certain boron and copper compounds are also capable of emitting green light.

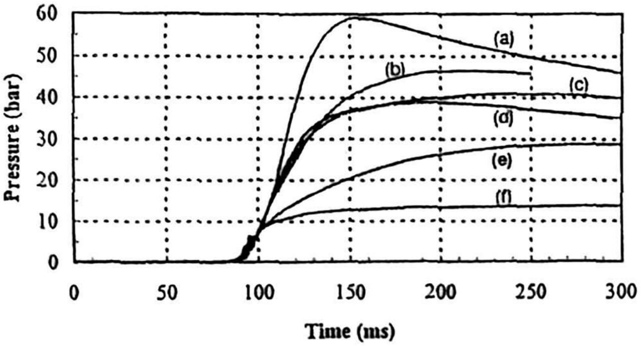

FIGURE 4.2 A time-vs-pressure (milliseconds vs bar) plot of a potassium nitrate/sodium azide system from closed-vessel experiments (Summer Pyrotechnic Seminars 2012). The oxidizer/fuel weight ratios are (a) 25/75, (b) 30/70, (c) 35/65, (d) 40/60, (e) 45/55, and (f) 50/50. Study shows that the 25/75 composition reaches the highest maximum pressure around the 150 ms mark, while others reach a reduced peak pressure at 175 ms or later in their reactions. These types of results could be used to "dial in" the right amount of pressure at the right time for an airbag system: too much pressure generated too fast could burst the containment bag, negating the cushioning effect. However, the right pressure but not produced quickly could mean that the airbag is not deployed and effective in time for its requirement.

VARIABILITY OF PYROTECHNIC COMPOSITIONS

To reproducibly create the desired pyrotechnic effect from a given mixture, the chemist must be aware of the large number of variables that can affect performance. These factors must be held constant from batch to batch and day to day to achieve reproducible behavior. Substantial deviations can result from variations in any of the following (Military Pyrotechnic Series Part One, "Theory and Application" 1967; Shidlovskiy 1964):

1. *Moisture*: The best rule is to avoid the use of water in processing pyrotechnic compositions and to avoid the use of all hygroscopic (water-attracting) ingredients. If water is used to aid in binding and granulating, an efficient drying procedure *must* be included in the manufacturing process. The final product should be analyzed for moisture content, if reproducible burning behavior is critical. Why is water so bad? The answer lies in several of the important physical and chemical properties of H_2O. Water is an excellent solvent for many polar and ionic compounds. If a component to be used in a composition is water-soluble, and water is used in manufacturing (such as to aid in activating a binder or in blending the composition), the water will dissolve some or all of the water-soluble material. Upon subsequent drying, the dissolved component will re-solidify, but it will almost certainly be a *different* particle size than the starting material that was first placed in the mixer. This can change both the performance and sensitivity of the composition. Water is also difficult to evaporate: it has a high heat of vaporization compared to other solvents, such as acetone, that are used to dissolve

binders or aid in mixing. A longer and perhaps warmer drying operation will be required to remove water (compared to a solvent such as acetone or ethyl alcohol, for example) following mixing and granulating.

If significant water remains in an energetic material in an end item, the water will absorb a significant amount of heat as it vaporizes during the burning of the composition. To put it another way, heat evolved from the ignition of material will go to evaporating water and not to heating and igniting unreacted material. This can and will hinder ignition and slow the burn rate of the composition. Finally, water is a reactive oxidizing chemical with fuels like magnesium, boron, and zinc. Residual water in a composition may slowly react with these fuels during storage—slowing up the burn rate of the composition, by a reaction such as

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 \tag{4.1}$$

and thereby creating performance problems. In this case, "optimal fuel" magnesium metal has been converted to "poor oxidizer" magnesium hydroxide. In addition, this reaction generates hydrogen gas that can cause a sealed device to bulge in storage and potentially ignite in the air, creating a further cascade of unintended consequences.

2. *Particle size of ingredients*: Homogeneity and pyrotechnic performance will increase as the particle size of the various components is decreased. The finer the particle sizes, the more reactive a particular composition should be, with all other factors being held constant.[3] Table 4.4 illustrates this principle for a sodium nitrate–magnesium flare composition. Note the similarity in performance for the two smallest particle sizes, suggesting that an upper performance limit may exist with respect to the metal fuel particle size. It is critical that a manufacturer have the in-house ability to measure and confirm the particle size of each new arrival of chemical material. Modern instrumental methods of analysis allow for the rapid and accurate determination of the distribution of particles in a chemical sample.

   The science and technology of particle size and particle shape analysis are topics worthy of their own books. For decades, particle sizes distributions were primarily measured using a "nest" of standard sieves, with the "holes" in the screens decreasing in diameter as you moved down the nest (see Table 4.3). A weighed sample of the chemical of interest was placed on the top sieve in the nest, a cover was put in place, and the nest was mechanically shaken for a specified period. The weights of the material that was held on each successively finer sieve in the nest were then measured, giving a distribution by weight per cent of the particle sizes in the sample.

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[3] Performance increases as particle size decreases up to a point for certain materials. In the case of aluminum, the protective oxide coating—the *surface area*—becomes a larger percentage of total mass—versus the *internal volume* of aluminum metal—as the particle size gets smaller. There is a point where an "aluminum" powder sphere is so small that there is very little actual aluminum metal—fuel—inside the aluminum oxide shell.

TABLE 4.3
Openings in U.S. Standard Sieves

Sieve Mesh Designation[a]	Sieve Opening in Microns
#20 mesh	841
#40 mesh	450
#100 mesh	150
#200 mesh	75
#270 mesh	53
#325 mesh	44
#400 mesh[b]	37

[a] The mesh designation is the number of openings per linear inch in the sieve.

[b] Material that passes through a #400 mesh sieve is very fine, but it still can be material that is up to 37 micron in size. Material in the 5 micron range cannot be analyzed with nay accuracy using sieves—an instrumental method is needed.

Newer instrumental methods of size analysis use a physical property of the particles in a sample, such as light scattering or sedimentation rate, to obtain a pattern of behavior for the sample. A programmed computer then takes the physical data and converts the observed behavior of the sample into a distribution of spherical particles, again by diameter, that would produce the observed pattern. This type of method can be quite good at comparing two samples (such as last month's shipment of metal powder and this month's shipment). If the two samples produce similar results in the analyzer, the two materials are likely to be similar in particle size and particle size distribution, and they should show similar pyrotechnic behavior. If the two results are quite different, differences in reactivity and sensitivity may be observed in energetic material made using the two materials. Also, it never hurts to have a microscope available to view the particles for shape—spheres, flakes, irregular granules, etc. Again, the important thing is similarity in appearance from drum to drum and shipment to shipment.

Particle size specifications often show up in either an "average" sizing or a distribution. There are many ways to obtain an "average" particle size; therefore, the method employed to obtain the reported particle size should be well understood in advance if different manufacturers are used for the same chemical with the "same" reported average size. A distribution plot can also be obtained, as noted above, for particle sizes. One of the components of a pyrotechnic mixture will show the greatest "particle size effect," often the metal or elemental fuel that melts or decomposes at the highest temperature (see Chapter 6 for the reasoning behind this).

3. *Surface area of the reactants*: While particle size is more easily measured, it is the actual *total surface area* that most affects burn rate. For a high-energy reaction to rapidly proceed, the oxidizer must be in intimate contact with the fuel. Decreasing the particle size of the components will increase

TABLE 4.4
Effect of Particle Size on Performance of a Flare Composition[a]

Composition	Component	% by weight	Average particle size
	Magnesium metal	48	See table below
	Sodium nitrate	42	34 μm (10^{-6} m)
	Laminac binder	8	–
	PVC	2	27 μm

Magnesium Average Particle Size, Micrometers	Flare Candlepower (1,000 Candles)	Flare Burning Rate, in./min
437	130	2.62
322	154	3.01
168	293	5.66
110	285	5.84

[a] Shidlovskiy (1964).

this contact, as it will increase the available surface area of the particles. A smooth sphere will possess the minimum surface area for a given mass of material. An uneven, porous particle (a Thomas English Muffin, so to speak—full of "nooks and crannies") will exhibit much freer surface per gram and consequently should be a much more reactive material than a smooth sphere of the same nominal particle size. Particle size is important, but it is the surface area that is truly critical in determining reactivity. Several examples of this phenomenon are presented in Tables 4.5 and 4.6.

4. *Thermal conductivity*: For a column of pyrotechnic composition to burn smoothly and rapidly, the reaction zone must readily travel down the length of the composition (whether vertically or horizontally). Heat is transferred from layer to layer, progressively raising the adjacent material to the ignition temperature of the composition. Good thermal conductivity can be essential for smooth propagation of burning, and this is an important role played by metal fuels in many mixtures. Metals are the best thermal conductors, with organic compounds ranking among the worst. Table 2.13 lists the thermal conductivity values of some common materials. Increase the thermal conductivity of a given composition, holding all other factors constant, and the burn rate of the material should increase.
5. *Outside container material*: Performance of a pyrotechnic mixture can be affected to a substantial amount by the type of material used to contain the mixed composition. If a good thermal conductor—such as a metal tube—is used, heat may be soaked up by the metal, carrying it away laterally from the composition through the wall of the container to the surroundings. The thickness of such a metal wall will also be an important consideration. If sufficient heat does not pass down the length of the pyrotechnic mixture, burning may not propagate, and the device will not burn completely. A worst-case scenario would be a thin column of a low heat output

TABLE 4.5
Effect of Particle Size on the Burning Rate of Tungsten Delay Mixtures[a]

	Mix A ("M 10")	Mix B ("ND 3499")
% Tungsten	40	38
% Barium chromate	51.8	52
% Potassium perchlorate	4.8	4.8
% Diatomaceous earth	3.4	5.2
Tungsten surface area, cm^2/g	1,377	709
Tungsten average diameter, 10^{-6} m	2.3	4.9
Burning rate of mixture, in./s	0.24 (faster)	0.046 (slower)

[a] Shidlovskiy (1964).

TABLE 4.6
Effect of Particle Size on Burning Rate[b]

Composition		
	Titanium metal	48% by weight
	Strontium nitrate[a]	45
	Linseed oil	4
	Chlorinated rubber	3

Titanium Size Range, Micrometers	Relative Burning Rate
Less than 6	1.00 (fastest)
6–10	0.68
10–14	0.63
14–18	0.50
Greater than 18	0.37 (slowest)

[a] Curiously, the system showed the *opposite* effect for strontium nitrate. Decreasing the particle size of the oxidizer from 10.5 to 5.6 μm produced a 25% decrease in burning rate.

[b] Thomson and Wild (1975).

composition inside a thick metal tube. Organic materials, such as cardboard, are widely used to contain low-energy pyrotechnic compositions (such as highway flare "fusees" and commercial fireworks) to minimize this problem (cardboard is a poor thermal conductor).

6. *Loading pressure*: There are two general rules to describe the effect of loading pressure—or consolidation—on the burning behavior of a pyrotechnic composition and the correct rule to use depends on the importance of the role played by hot gases in propagation of the reaction. In the first case, if the pyrotechnic reaction, in the post-ignition phase, is largely propagated via hot gases penetrating forward into the unreacted material, then a high loading pressure will reduce the porosity of the composition and retard the passage of these hot gases down the column of composition. This means

TABLE 4.7
Effect of Loading Pressure on the Burning Rate of a Delay Mixture

Composition[a]		
	Barium Chromate	90
	Boron	10

Loading Pressure (1,000 psi)	**Burning Rate (s/g) (Shidlovskiy 1964)**
36	0.272 (fastest)
18	0.276
9	0.280
3.6	0.287
1.3	0.297
0.5	0.309 (slowest)

[a] This is a "gasless" delay mixture—the burning rate increases as loading pressure increases. "Gassy" mixtures will show the opposite behavior.

that a *lower* burn rate, in units of grams of composition reacting per second, will be observed at high loading pressures.[4] In the second case for low-gas or "gasless" compositions, particle-to-particle contact is the primary means of heat transfer. This type of system will show the opposite effect upon consolidation—this will have a *higher* burn rate in units of grams/second—as the loading pressure increases. Table 4.7 illustrates the effect of loading pressure on the burn rate of a low-gas boron–barium chromate composition; note that the rate is listed in units of seconds/gram, and the *smaller* number means the fastest rate.

Of course, no composition is ideal, and many mixtures will have a varying combination of both "hot-gas" and "surface-contact" means of heat transfer. The loading pressure may both advance and inhibit burn rate depending on the parameters involved.

7. *Degree of confinement*: In Chapter 1, the variation in the burning behavior of black powder was discussed as a function of the degree of confinement. Increased confinement leads to accelerated burning almost universally. Shimizu reports a burning rate in air of 0.03–0.05 m/s for black powder paste impregnated in twine. The same material, enclosed in a paper tube of 1 cm inside diameter, had a burning rate of 4.6–16.7 m/s—*over 100 times faster* (Shimizu 1982). We can suppose the major effect is at work here: as noted above, significant hot gases will be generated with black powder that will disperse through the unreacted material (and not to the open atmosphere where the heat would dissipate), which pre-heats the material to the ignition point, accelerating the rate substantially. This behavior is typical of confined loose powders and points out the potential danger of confining mixtures that burn somewhat sluggishly in the open air.

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[4] One must always be cautious in interpreting burn rate data versus loading pressure, because an increase in loading pressure should logically lead to an increase in the density of the composition. What may appear to be a slower rate, expressed in units of mm/s, may actually be a faster rate in terms of grams per second.

> This effect is particularly important when consideration is given to storage (since nearly all components and mixtures are stored in sealed containers to safeguard from ambient conditions and accidental spills), as well as for the selection of manufacturing equipment for pyrotechnic compositions. Equipment for the processing of energetic material—such as mixers, granulators, and dryers—should be vented to ambient pressure. The equipment may not come from the manufacture with pre-installed pressure-relief vents or valves as a standard feature, certainly not if the equipment is not normally sold to manufacturers of energetic materials. For processing foodstuffs, medicines, and other non-energetic material, purity and hygiene are the foremost considerations, and the equipment is often designed to be tightly sealed during operation to keep out contaminants (mice, roaches, or flies, for example). Storage containers, workrooms, and storage facilities for energetic materials must be designed to rapidly vent, in case of an ignition that leads to pressure buildup. Such venting is designed and intended to prevent a fire from progressing to an explosion. Several factors contribute to the effect of confinement on burning rate. First, as was discussed earlier in Chapter 2, an increase in temperature produces an exponential increase in the rate of a chemical reaction. In a confined high-energy system, the temperature of unreacted material can rise dramatically should an ignition occur (remember the hot gases), as heat is not effectively lost to the surroundings. A sharp rise in reaction rate occurs, liberating more heat, raising the temperature further, accelerating the reaction until an explosion occurs or the reactants are consumed. To put it another way, in a confined system, the hot gases that are produced cannot escape and will consequently build up substantial pressure, holding heat at the burning surface and driving the hot gases into the high-energy mixture, thereby causing an acceleration of the burn rate. The minimum quantity of material needed to produce this kind of explosion, under a specified set of conditions, is referred to as the *critical mass*.

In summary, the burning behavior of a composition/system can be summarily affected by two broad parameters: homogeneity and confinement. An increase in either should lead to an increase in burning rate for *most* high-energy mixtures. However, again, it must be noted that "gasless" compositions do not show the dramatic confinement effects found for "gassier" compositions. Burn rate will be discussed further in Chapter 6.

REQUIREMENTS FOR A "GOOD" HIGH-ENERGY MIXTURE

The requirements for a commercially feasible high-energy mixture are outlined as follows, keeping in mind the preceding discussion of factors that affect performance:

1. Effect: The composition produces the desired effect.
2. Efficiency: The composition is efficient both in terms of effect-per-gram as well as effect-per-dollar.

3. Simplicity: The composition can be manufactured without any expensive or unique equipment but with a minimal number of complicated or technical procedures.
4. Safety: The composition can be safely manufactured, handled, transported, stored, and used, assuming normal treatment and the expected variations in temperature.
5. Sensitivity: Ignition is consistent and reliable, and sensitivity to ignition meets acceptable criteria for both safety and performance.
6. Storage: Storage lifetime is acceptable, even in humid conditions.
7. Toxicity: There is reasonably low toxicity and adverse environmental impact associated with both the starting materials and reaction products.

These requirements seem rather simple and in many cases obvious, but they do restrict or eliminate a number of potential starting materials for one or several of the factors noted above. For example, the compounds below must either be deleted from the "acceptable" list or special precautions must be taken in order to use them when absolutely justified. These examples include:

Potassium dichromate ($K_2Cr_2O_7$): This is a strong oxidizer but contains only 16% oxygen by weight (inefficient). It has a corrosive effect on the mucous membranes (toxic), and its suspected carcinogenicity advises the use of alternate oxidizers. It is one molecule in the family of "hexavalent chromium" compounds that have received considerable adverse publicity.

Ammonium perchlorate (NH_4ClO_4): This is a good oxidizer and can be used to make excellent propellants and colored flames. However, it is a self-contained oxidizer-fuel system much like ammonium nitrate (safety), poses potential explosive behavior in large quantities (storage), and is a member of the "perchlorate" family (toxicity).

Perchlorates in general ($X^+ClO_4^-$): The various perchlorates, such as potassium perchlorate ($KClO_4$) and ammonium perchlorate (NH_4ClO_4), used in solid propellants and pyrotechnics have been under great scrutiny as a possible source of groundwater contamination, as discussed earlier (toxicity). Once rated among the "ideal" oxidizers, the perchlorates are now being avoided in the development of new energetic materials wherever possible.

Magnesium metal (Mg): This is an excellent fuel and produces brilliant illuminating mixtures. The metal is water-reactive, however, suggesting short shelf life and possible spontaneous ignition if magnesium-containing mixtures become wet (storage, safety). Whenever possible, replace magnesium with the more stable aluminum or "magnalium" alloy of aluminum with magnesium. If magnesium gives the best effect, and must be used, the metal can be found coated with an organic, water-repelling material.

Zirconium metal powder (Zr). This material is associated with world-record spark sensitivity and explosive behavior when mixed with an oxidizer (safety). Use it only when you need flame temperatures and reaction products in the 4,000°C and above range. Advanced precautionary procedures should be used when handling zirconium powder, especially when blending with oxidizers: extra protective equipment for the hands and face, mixing as little as possible at one time, with remote-mixing if at all possible.

PREPARATION OF HIGH-ENERGY MIXTURES: AN INTRODUCTION

Although this will be discussed in-depth in the following chapter, it bears discussing an introduction to preparation of pyrotechnic compositions in light of the pyrotechnic principles just outlined in this chapter. The most hazardous operations in the high-energy chemistry field involve the mixing of oxidizer and fuel in large quantities and the subsequent drying of the composition (if water or other liquid is used in the mixing and granulating processes). In these operations, large quantities of bulk powder are present in one location, and if accidental ignition should occur, there is a good chance that an explosive reaction rate may be reached.

For this reason, mixing and drying operations should be isolated from all other plant processes, and remote-controlled equipment should be used wherever and whenever possible, using video technology for surveillance of the operation. All high-energy manufacturing facilities should be designed with the idea in mind that an accident will occur at some time during the life of the facility. The plant should be designed to minimize any damage to the facility, to the neighborhood, and most importantly, to the operating personnel—should an incident occur (Department of Defense Explosives Safety Board 2008). The manufacturing operation can be divided into several stages:

1. *Preparation of the individual components*: Materials to be used in the manufacturing process may have to be initially dried, as well as ground or crushed to achieve the proper particle size and screened to separate out large particles or foreign objects. Oxidizers should never be processed with the same equipment used for fuels nor should oxidizers and fuels be stored in the same area prior to use. All materials must be clearly labeled at all times.
2. *Preparation of compositions*: This step is a major key to proper performance. The more homogeneous a mixture is, the greater its reactivity will be. The high-energy chemist is always walking a narrow line in this area, however. By maximizing reactivity—with small particle sizes and intimate mixing—you are also affecting sensitivity and increasing the chance of accidental ignition during manufacturing and storage. A compromise is usually reached involving careful specification of particle size, purity of starting materials, and safe operating procedures. Follow all standard operating procedures.
3. *Mixing*: A variety of methods can be used for mixing. Materials can be blended through wire screens, using brushes. Hand-screening has been used in the fireworks industry but should never be used with explosive or unstable mixtures. Brushes provide a safer method of screening the oxidizer and fuel together. Materials can also be tumbled together in a closed container to achieve homogeneity, and this can (and should) be done remotely. Remote mixing, and barricading, is strongly recommended for sensitive explosive compositions such as the “flash and sound” powder used in firecrackers and salutes and the photoflash powders used by the military. For some of these compositions and devices, it is possible to add the oxidizer

and fuel(s) in separate increments, and then tumble the end items (remotely) to achieve blended composition in the end items. This procedure enables the manufacturer, when possible, to avoid having to mix larger bulk quantities of a sensitive, explosive powder. For small amounts of relatively safer compositions, the material can be blended by manual stirring in a dish or a cup, with proper safety precautions against unwanted ignition.

4. *Granulation*: Following mixing, the powders are often granulated, generally using a small percentage of binder to aid in the process. The composition is treated with water or an organic liquid (such as alcohol or acetone) to activate the binder and then worked through a large-mesh screen (*note*: composition that is blended with the aid of a binder–solvent solution can proceed directly to the granulation stage after mixing). Grains of well-mixed composition are produced which will retain the homogeneity of the composition better than loose powder. Without the granulation step, light and dense materials might segregate during transportation and storage, and dust generation is likely. The granulated material is dried in a remote, isolated area and is then ready to be loaded into finished items. Remember: Sizable quantities of bulk powder are present at this stage, and the material must be protected from heat, friction, shock, impact, and electrostatic spark. As an alternative to granulation, extrusion of paste-like composition can be done with many compositions, using equipment specifically designed with energetic materials in mind. This process permits the formation of specific geometric shapes for the finished grains of composition. Venting is of particular importance with this type of equipment.
5. *Pressing/Loading*: An operator, working with the minimum quantity of bulk powder, loads the composition into tubes or other containers or produces pellets for later use in finished items. The making of "stars"—small pieces of color-producing composition used in aerial fireworks, distress flares, and illuminant signals—is an example of this pelleting operation. Loading pressure, dwell time, barricading, and equipment maintenance are all critical factors in pressing operations (Department of Defense Explosives Safety Board 2008).
6. *Testing*: An important final step in the manufacturing process is the continual testing of each lot of finished items to ensure proper performance. Significant differences in performance can be obtained by slight variation in the particle size or purity of any of the starting materials, and a regular testing program as part of the manufacturing process is the only way to be certain that proper performance is being achieved.

VARIATION FROM DAY TO DAY

Pyrotechnic compositions in particular have acquired a reputation for variability in manufacturing—compositions made on Monday will occasionally not behave the same as compositions made on Thursday. "Why" is always the question, and the source can be any one of a number of individual factors discussed previously in this chapter or a combination of several factors. Troubleshooting (in addition to a Process

Hazard Analysis, see Chapter 5) is a part of the life of anyone who is involved in manufacturing pyrotechnics.

The list of likely suspects always includes particle size variation, moisture, and chemical purity, as well as each stage in the manufacturing process. Establishing and maintaining good-quality control procedures on incoming shipments of chemical components is critical. The following is a checklist developed a number of years ago in a discussion at one of Dr. John Conkling's Summer Pyrotechnic Seminars held at Washington College in the "eastern shore" town of Chestertown, Maryland. This was done in an effort to identify places in the manufacturing process where variation in end item performance might result if any deviation from the standard operating procedure occurs. Hopefully, this chart might possibly serve as a checklist for someone trying to identify a possible source of variation in pyrotechnic/propellant performance.

POSSIBLE AREAS WHERE VARIATION IN THE PERFORMANCE AND SENSITIVITY OF PYROTECHNIC MIXTURES CAN OCCUR DURING THE MANUFACTURING PROCESS

- Starting chemicals—purity, age, contamination, residual moisture, surface coating
- Particle size/shape (surface area)
- Variation by particle size of chemicals within a drum (due to settling)
- Drying of individual materials (prior to weighing)
- Formula (% change)—an intentional change to alter performance
- Evaporation of solvent in binder solution
- Weighing of chemicals (accuracy of scales)
- Amount actually delivered to the mixer (spills, residual in containers, etc.)
- Introduction of foreign material/moisture throughout the process
- Mixing—type of mixer used and method
- Mixing time, speed, energy (does mixing process affect particle size?)
- Sequence of chemical addition to the mixer
- Solvent evaporation rate in the mixer
- Humidity and temperature in mixer/mixing area
- Granulation—final grain size of blended mix
- Drying of blended mixture—% residual solvent/moisture

  (At this stage, initial performance tests are typically run on the mixture; if it meets specifications, it proceeds to the loading area. Otherwise, it is reworked, cross-blended, or destroyed.)
- Storage (prior to loading)—exposure to moisture or decomposing heat
- Loading/Pressing—loading pressure, dwell time
- Loading—number of increments
- Loading—amount of fill (bulk volume vs. total mass);
- Hardware variation—size of parts, seals in end items;
- Wall thickness and venting pressure of a confinement tube/vessel
- End item storage/treatment/handling
- External temperature and pressure when the device is ignited

AGING EFFECTS ON PYROTECHNIC COMPOSITIONS

It is expected that the chemicals used to make pyrotechnic compositions and even the mixed compositions themselves may have to be stored for unknown or extended periods of time. However, it may also be expected that the materials will still perform as originally intended even after storage and aging. Different chemicals will age differently in storage than others, subject to such processes as oxidation (such as at the surface of metals), breakdown from heating (such as for nitrocellulose), or denaturing from the presence of acids (such as for more complex organic chemical used as colored dyes).

Studies can be undertaken to determine:

1. If there is a chemical change over time
2. The cause of the change
3. The change on the performance of the pyrotechnic mixture
4. If anything can be done to mitigate the change
5. The useful lifetime of a pyrotechnic chemical or mixture under certain storage conditions

Researchers will have to study both "fresh" compositions as well as the aged composition with analytical instrumentation as well as observe performance to understand aging effects. Results such as the chemical makeup, the heat of reaction, ignition temperature, burning time, light/color output, and sound output are all factors that can change over time as a pyrotechnic composition ages. While some inferences can be made (fresh metals will form an oxide layer, carbonates might lose carbon dioxide to form oxides), the only way to truly understand the aging effects of a specific mixture is to study it directly.

An example analytical process was presented on the aging effects of an output charge that was intended to ignite the main gas generator in a military munition (de Klerk, Berger, and van Ekeren 2008). The igniter composition was comprised of boron, potassium nitrate, and nitrocellulose, along with an epoxy resin (as a binder to keep the material together) and polyamide thermoset used to cure the resin. The boron and potassium nitrate were used as the high temperature igniter with the nitrocellulose to generate gas and disperse the hot particles onto the next stage to ignite the material. While B/KNO_3 is thermally stable, potassium nitrate is hygroscopic and will slowly absorb moisture (which can retard the burn rate, swell the epoxy, or introduce acids), and boron can take on acid to form boric acid (eliminating the necessary fuel material). Furthermore, nitrocellulose undergoes thermal decomposition, releasing nitrogen oxides that can affect the epoxy resin and any brass that is used the housing. Analysis of an artificially aged system found that, as expected, performance degraded with age.

If a material is to be stored for any period of time, or if the chemicals used to make mixtures are to be stored and used over a long period of time, understanding how age can affect performance is an extremely important principle for pyrotechnic researchers. Care should be made to understand how a material ages, what the age effect will be, and any mitigation that can be done to slow the process.

PYROTECHNIC PRINCIPLES: A FINAL NOTE

Pyrotechnic practices can be thought of as a "culinary" method, in that the ingredients must be right, but the technique of the cook must also be astute. For both cooking and pyrotechnics, these crafts combine rigorous scientific understanding (e.g., how chemicals react at the molecular level) as well as more esoteric insight from the wisdom of the performer (e.g., knowing how processing may affect storage lifetime for eventual use). A skilled pyrotechnician has a broad and deep understanding of the chemistry, principles, technical parameters, hazards, sources of variation, and best practices for their trade.

To quote the poetic verse of Takeo Shimizu in his seminal text *Fireworks from a Physical Standpoint*, as translated by Alex Schuman: "The nature of the beauty of fireworks lies in the temporal and spatial ('break') effect that they have on our minds… In order to create such beauty, one must first thoroughly learn the burning appearance as well as the properties of the chemical compositions" (Shimizu 1982).

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5 Pyrotechnic Laboratories and Analysis

HAND MIXING: For many centuries, and still today, many pyrotechnic compositions were gently blended by hand through a screen to produce a homogeneous material. Modern mixing equipment has removed personnel from the immediate mixing area, due to concerns over accidental ignition from friction and spark.

Probably beginning with the discovery and early manufacture of original black powder, proto-pyrotechnicians were producing and evaluating their compositions with a set of customized tools in dedicated spaces: what we would now call "laboratories." Indeed, laboratories today are still dedicated, highly customized spaces with specialized tools and equipment intended for scientific discovery. Once manufactured, these early pyrotechnicians needed to evaluate their products, often simply by observing how well the reaction completed the intended effect. Today, technological progress has afforded pyrotechnicians not only invaluable types of tools to create pyrotechnic compositions based on the creator's needs and preferences but also numerous analytical systems to precisely investigate both the compositions as well as measure their effects.

INTRODUCTION

One question that is frequently asked with respect to the study of energetic materials deals with the type of equipment that a researcher or manufacturer should have for research as well as quality control use. Scientists need to not only have the ability to store and safely handle the chemicals in question for creating pyrotechnic mixtures but also safely produce them (separating particle sizes, weighing, mixing, packaging, etc.) and then objectively measure their resulting reactions: burn rate, light output, gas/smoke output, color or sound intensity, etc. Furthermore, what if the output is not as intended, should the researcher go on guessing at the problem and its remedy or instead use a wide array of available analytical tools to investigate and hypothesize on the root cause and solution to the issue?

While we briefly discussed preparation of pyrotechnic compositions in relation to pyrotechnic principles in the previous chapter, this chapter will provide a further discussion of pyrotechnic laboratories, some tools used in the small-scale production of energetic compositions for research, analytical methods, and equipment that can assist the pyrotechnician and several notes on best practices for safety and quality control.

It must be stressed that *THIS BOOK IS NOT INTENDED TO BE, AND IS NOT A COMPREHENSIVE TRAINING COURSE ON SAFELY PREPARING, HANDLING, OR IGNITING PYROTECHNIC MIXTURES.* As we have already seen, energetic materials can be quite harmful simply as a result of their intrinsic nature and therefore only formal, vetted, and verified training generated by accredited groups and given by skilled and experienced pyrotechnic experts should be sought and completed before beginning any work with pyrotechnics in a setting where experts can oversee the novice's work. These can include training courses by government, industrial, and academic organizations involved in propellants, explosives, and pyrotechnics, as well as national and international hobbyist groups such as the Pyrotechnics Guild International (PGI) and any number of local hobbyist organizations.

Furthermore, federal, state, and local laws may place restrictions on the preparation of energetic mixtures by individuals—such as requiring special licenses, storage requirements, or other certifications. Joining a group such as the Pyrotechnics Guild International, as well as a local affiliate group of people with an interest in the art and science of pyrotechnics is recommended for anyone interested in pursuing an interest in the field of pyrotechnics.

THE PYROTECHNIC LABORATORY

"Laboratory" comes from the Latin "laborare," which means "to do work." Nowadays, a laboratory is a dedicated space for technical research and investigation into particular scientific phenomena, ideally under conditions that are as controlled as possible that contains all the necessary tools, equipment, and features to adequately support the scientific exploration. In the case of pyrotechnics, this also means a place to store the amount of chemicals needed for producing pyrotechnic compositions but only in the smallest necessary quantities, with bulk materials stored off-site in dedicated, secure containers.

The laboratory should be clean, well-lit, and climate-controlled to regulate, as well as possible, the temperature and humidity of the ambient air. Dehumidifiers are common in pyrotechnic laboratories, recalling the key axiom "keep your powders dry" to minimize unwanted degradation of performance or reaction by water/acid-sensitive chemicals. Large ovens are also common, set to temperatures above the boiling point of water but often below the melting/ignition temperature of any mixtures being manufactured. This allows for chemicals, mixing tools, and storage equipment to be fully dried before their use.

Many laboratories also now use conductive flooring connected to an outside electrical grounding wire to remove unwanted static electricity. As we will see in Chapter 7, static electricity discharge can be a major hazard in inadvertent ignition of compositions, especially ones containing powdered metal.

At least one sink should be present in the laboratory for the worker to be able to wash their hands (or face/eyes if needed) as well as any equipment used in weighing, mixing, or storing other chemicals. However, there are very strict rules on what chemicals can be washed down the sink to normal sewer systems, and almost all laboratories have dedicated "waste bins" for both solid and liquid chemical waste. Drying racks for allowing equipment to air dry are usually near the laboratory sink.

Access to the space should be controlled via locked doors, ideally with a window on the doors for emergency personnel to see inside as needed. Two or more means of egress, such as doors or windows to fire escapes, are essential in the case of pyrotechnic laboratories. It should be assumed that an accident will result at some point, and one must plan for all contingencies in case.

The laboratory should have fire suppression systems, based on the nature of the compositions being mixed; this often means water-sprinkler system but may also mean more intensive suppression systems in the case where highly energetic or water-sensitive compositions are present. Remember, since pyrotechnic mixtures contain oxidizers, they do not need atmospheric oxygen to burn, and water may not always be enough to quench or smother a burning pyrotechnic.

STORAGE

The laboratory should have adequate benchtop space for supporting equipment as well as storage space, such as cabinets, for storing chemicals and equipment. Some of these cabinets can be normal wooden cabinets with shelves, others with glass/clear fronts for the scientist to see the contents inside, while other should be metallic, depending on the nature of their contents. In the case where *mixed* energetic materials are stored, which includes fuses and matches in addition to mixes, those should be kept in specialized, sealed metallic cabinets or containers that can handle any resulting fire or blast. Organic (flammable) solvents should be kept in specialized metallic cabinets.

Storage of solid chemicals in cabinets should be controlled and inventoried and always stored "like with like." Oxidizers should be stored with other oxidizers, metals with metals, other/organic fuels with other/organic fuels, and other additives stored as is most efficient. Each chemical should be inventoried and the full properties understood via a Material Safety Data Sheet, or "MSDS," which will detail any hazards and chemical incompatibilities. For example, even though ammonium nitrate and potassium chlorate are both oxidizers, accidental mixing and the presence of a catalyst can convert AN to ammonium chlorate—an unstable and potentially explosive compound. One should be sure to keep those two oxidizers separate. Copies of the MSDS should always be kept on-site or readily available.

Storage of powdered chemicals can be done in suitable containers that allows for "air tight" storage as well as easy ability to extract the chemicals. One common type of storage container is the "Nalgene®" brand of bottles and jars, originally manufactured for laboratory use but now commonly seen in branded water bottles and liquid containers. Bottles such of these should have screw cap or sealing "pop top" lids, allow for air-tight sealing, be chemically inert or resistant, and have large wide-mouth openings to make scooping out or pouring out the solid chemicals relatively easy. Figure 5.1 shows a classic opaque plastic Nalgene-type bottle used to store bulk fuse (that can be pulled and cut-to-measure). In the case where the chemicals will degrade plastic, glass or ceramic jars with gasket-sealed lids are also viable. Very rarely are metallic bottles used, as the metal can catalyze reactions or even react with the chemicals inside.

One safety note on using bottles for storage: Errant material can sometimes get caught in the cap area or lid, which can then lead to materials being "ground together" as the cap is closed. This is an example of friction stimulus, discussed in Chapter 7, and can lead to unexpected ignition of certain materials, certainly if the bottle contains mixed pyrotechnics. Care should always be taken to ensure the cap area and lid are clear of solid materials before closing.

Pyrotechnicians will typically label their powders both by chemistry but also by size and type, manufacture date to understand any aging issues, and other particulars. For example, a bottle labeled "aluminum" could mean any kind of form, size,

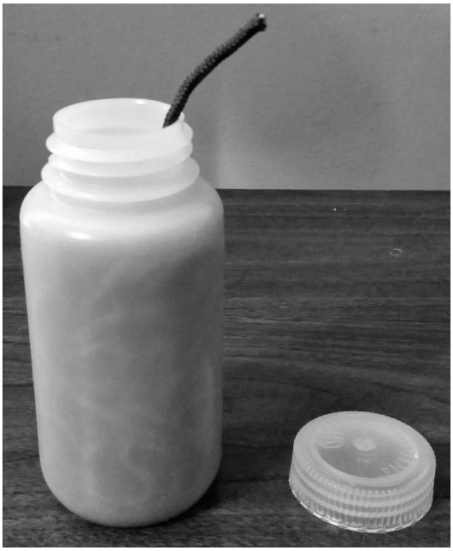

FIGURE 5.1 A 250 mL "Nalgene" brand plastic screw-cap bottle used for storage of pyrotechnic chemicals and materials. This bottle contains a long length of pyrotechnic fuse that can be easily pulled and cut to length as needed. When not in use, the cap is screwed on tight to keep out moisture or any errand flying hot particles or sparks that could ignite the entire fuse. Since a fuse is an active pyrotechnic, when not in use, the bottle is sealed and stored in a fireproof container.

or coating. However, a bottle labeled “Aluminum powder, Conkling-Mocella Pyro Co., Spherical, German blackhead, January 2010, –325 mesh” tells us that it is aluminum in powder form (vs flake form), was made by the “Conkling-Mocella Pyro Company[1],” the particles are spherical (vs rougher granular types), it is coated in the German blackhead process, was made in January 2010, and the size is –325 mesh (see below). Quite a bit of good information!

Extra safety storage of bottles of chemicals can be achieved using “magazine” style metal boxes, similar to those used by armed forces for transportation of ammunition and ordnance. These can be bought directly from manufacturers and also found at military surplus stores.

Storage of waste before disposal is a serious component of any chemical laboratory. Each country, state, and even local town has their own laws and regulations for what chemicals can and cannot go “down the drain” for waste removal: potassium nitrate (saltpeter) might be fine, potassium perchlorate is certainly not. Usually solid waste bins as well as liquid waste “carboys” are present in safe locations for the disposal of waste. Organic solvents with dissolved chemicals often go in one liquid waste container, with aqueous (water) waste in another. Even the ash from burned pyrotechnics, depending on the starting material, may have to go into specific waste storage (and not the usual trash) depending on the starting materials. For example, as we have seen, perchlorates can persist in the environment and cause harm when unreacted/unburned; cleaning any solid residue and disposing through environmentally friendly means is the best course of action.

Storage of personal items for the working scientist is also valuable, such as a place to leave personal items when working, and a place to leave laboratory personal protective equipment (or PPE) when finished for the day. These should be kept as far away from the working area, or even outside of the laboratory, to avoid any unwanted consequences. Food or drink should not be allowed in the laboratory. The risk of contamination is too great. Even closed drinking water bottles should be kept outside of the laboratory. (One often knows if a laboratory building is occupied and being used if water bottles line the spaces outside of laboratory doors down the hallway!)

Of course, no scientific laboratory today is complete without a telephone (be it a wireless/cellular telephone or classic landline) and a computer with Internet access. Computers will not only be useful to record results and research information but are often the interface to control and record data from sophisticated analytical equipment.

It can also be helpful to have a microscope with camera available to study and photograph the particles in question. Particles come as spheres, rods, plates, flakes, and other geometries—a change in the shape of your particles could affect their reactivity, as well as the sensitivity of mixtures produced with the material. If a chemical has changes in its particle size or shape from one shipment to the next, careful evaluation of the material is required before it is put into production.

SAFETY: PERSONAL PROTECTIVE EQUIPMENT AND COMMON PRACTICES

Safety is of the utmost concern for pyrotechnicians and anybody nearby to their activities. Loss of life and property are avoidable events, if proper safety precautions and practices are undertaken to include the necessary equipment.

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[1] It goes without saying: a fictitious company.

A comprehensive safety plan is critical for all pyrotechnic laboratories. These plans will include identifying all of the materials, equipment, and work to be done in the laboratory as a starting point. Additionally, the plans will then identify the hazards associated with the chemicals, equipment, and work to be done and how those hazards can be mitigated. Finally, specific plans for performing the work to be done will be addressed, along with methods for reporting any hazard issues that arise to refine the safety plans. A joint editorial by pyrotechnicians at Texas Tech University and the Lawrence Livermore National Laboratory outlined one approach in this area (Pantoya and Maienschein 2014).

Personal protective equipment (PPE) should be worn at all times when working with or around energetic materials. This means durable, non-flammable closed-toed shoes, with boot being preferred. Boots that interact properly with conductive flooring noted above are common in large-scale facilities. Hats can be worn to protect flammable hair from flying sparks and hot particles, with long hair being secured underneath. Long pants are essential. Flame-resistant lab coats, long-sleeved, are necessary when working with pyrotechnics (which are more durable against burning that the typical white cotton-blend lab coats). These lab coats should be fully enclosed with the buttons/zippers available. The sleeve enclosures should be as closed as possible while still allowing the worker to operate. (Specialized blast-suits, seen with bomb squads and explosive ordnance disposal EOD units are also used in the high-explosive industries but are out of the scope of this text.)

Eye protection is a must at all times in the pyrotechnic laboratory and should be worn immediately upon entering the laboratory even if no work or events are happening. Eyesight loss is a preventable, but often irreversible, hazard in any laboratory. Full enclosure around the eyes is required, more than what common reading glasses provide. Since shooting sparks and flying hot particles are a central part of pyrotechnics (remembering “Murphy’s Law” that anything that can go wrong, will go wrong): burning particles *will* find their way into any unprotected spaces.

Since hands and fingers are used to mix chemicals, hold tools, and operate equipment, basic hand protection is vital. Standard disposable synthetic gloves, such as vinyl or nitrile gloves, should be abundant. These can afford some protection against hot particles, as well as protection against harmful chemicals getting to the skin and causing surface chemical burns, or even getting through the lipid bilayer of the skin and into the blood stream. Extra protection for the hands against hot materials and fire is also crucial in the form of very thick laboratory heat-resistant “hot gloves” that are able to resist flames and the heat of materials up to a certain temperature, in some cases even a few thousand degrees Celsius.

COMPOSITION PRODUCTION

When a suitable laboratory space is ready and the chemicals are acquired, the work can begin to test out new compositions. The pyrotechnic chemist always begins with a very small quantity of composition when carrying out initial experiments on a new formula. The preparation of one or two grams of a new mixture enables one to evaluate performance (color quality and intensity, smoke volume, etc.) without exposure to an unduly hazardous amount of material.

SIZING PARTICLES AND POWDERS

If powders have not already been "sized" to the desired amount, a mesh screen "sieve" system can be used, such as a sieve shaker. Mixtures of the same chemicals with different particle sizes will behave very differently and therefore specific sizing is often required. Sieve bowls can be stacked in a "shaker" to appropriately separate different sizes of particles based on whether they fall through the holes in the sieve screens or not. An example sieve shaker is shown in Figure 5.2.

Mesh screens are given a "mesh number" in the American Society for Testing and Materials (ASTM) E-11 "Standard Specification for Woven Wire Test Sieve Cloth and Test Sieves" system, which is based on how many holes per linear inch of screen. For example, a "270 mesh" sieve has approximately 270 holes per linear inch

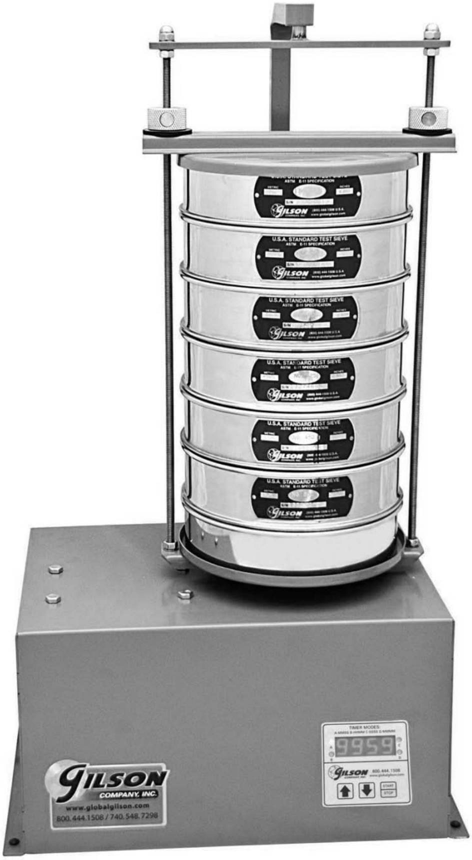

FIGURE 5.2 An automatic sieve shaker. The device will take sieves of different mesh sizes—larger opening at the top with each lower sieve having smaller openings then the one above—and shake them as a stack in three directions to allow smaller particles to work their way down the sieves, with larger particles retained on the top sieves. Image courtesy: Gilson Company, Inc. (https://www.globalgilson.com).

of screen. Therefore, larger mesh numbers mean smaller holes (more holes per inch) and only smaller particles fall through, while smaller numbers mean larger holes (fewer holes per inch) and large and small particles will fall through. If powders are run through a particular sieve, the material that falls through is considered –270, or "minus two-seventy," while the material on top that does not fall through is +270, or "plus two-seventy." In a dual system of a 270 mesh on top of a 325 mesh (even smaller holes than the 270) sieve, those that fall through the 270 screen but not the 325 mesh screen are –270/+325, or "minus two-seventy, plus three-twenty-five" and all particles present are pretty close to the same sizing. Table 5.1 shows the correlation between mesh number, the size of the holes in "microns" (another name for micrometers, which are one-millionth of a meter), and inches.

If the particles need to be at a particular size (such as –270 mesh), but the bulk material is larger particles, the pyrotechnician will need to grind up or otherwise make the particles smaller. This can be done "the old-fashioned way" with a mortar and pestle (grinding particles by hand) or by using a more-modern automatic "bead mill" or "ball mill." The latter systems are usually a thick ceramic container with a tight-fitting top and gasket to which the powder is added along with several ceramic "beads" or balls. The bead mill will be put onto its side on top of a rolling tray which will spin or roll the mill at a speed that allows the beads and powders inside to move around but also so the beads will be pulled up and fall back down (i.e., not subject to full centripetal force and just keep spinning around the inside of the mill). This creates a system where beads are constantly falling on top of the powder in the closed container, hopefully breaking up the particles into smaller sizes. The mills usually need to be left for some time to do their work (or overnight), but once done, the powder can be processed through a sieve shaker and the powders can be sized accordingly.

TABLE 5.1
Comparison of Mesh Number with Hole Sizes in Microns and Inches[b]

Mesh Number[a]	Hole Size in Microns	Hole Size in Inches
20	841	0.0331
30	595	0.0232
40	400	0.0165
80	177	0.0070
120	125	0.0049
170	88	0.0035
200	74	0.0029
270	53	0.0021
325	44	0.0017
400	37	0.0015

[a] Only a select number of mesh numbers are shown for simplicity.

[b] ASTM International (2017).

MEASURING CHEMICALS

Once the powders are sized and ready, a balance or laboratory scale will be used to weigh out the proper amounts of chemicals needed. Digital scales are quite common and should be calibrated on a regular schedule to ensure proper weighing. Once the first chemical is selected, a scoop, spatula, or other device can be used to transfer the powder from the main storage container into a bowl, cup, or other container for measurement. Pyrotechnic chemists often like ceramic bowls (sometimes called evaporation dishes based on their other use) or other smooth-surfaced bowls that allow for mixing with reduced risk of grinding and frictions against a rougher surface. Other convenient disposable containers are small paper cups (like the ones found at water coolers). Be sure to find ones without waxed surfaces, as the wax can be pulled off and blended into the mixture inadvertently. Figure 5.3 shows large particle-sized magnesium (dark particles) and sodium nitrate (white particles) inside a paper cup, mixed as well as possible; the large particle size was intentional in this case for a specific demonstration.

To avoid cross-contamination of chemicals, the scoop should only be used for *one chemical* and not on several containers. Even small amounts of cross-contamination from unclean scoops can cause catalytic changes in bulk material. Furthermore, cross-contamination of fuels and oxidizers can lead to unintended ignition and the possibility of a cascade chain reaction igniting other nearby pyrotechnics. Another good tip for weighing out powder is to use different containers for each chemical to be weighed: the possibility exists of over-adding too much of one powder to another, and there is no simple way to cleanly remove one powder from a container of two or more.

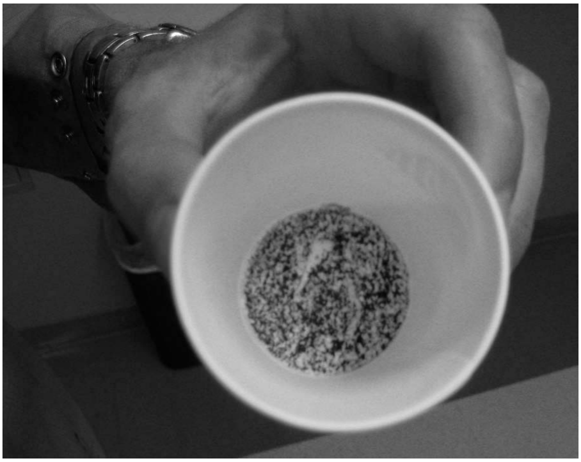

FIGURE 5.3 A common paper cup used as a mixing container for large particle-sized magnesium (dark spots) and sodium nitrate (white spots). Unwaxed paper cups are common for dry-mixing vessels in small-scale pyrotechnics: The material is non-reactive, inexpensive, and disposable. Furthermore, any leftover active pyrotechnic composition material stuck on the paper cup can be disposed of by burning the cup itself in a safe manner.

Selection of the sample from a container is, of course, very important. Since the sample taken from a container should be wholly representative of bulk material it was taken from, a good "best practice" before measuring chemical is to tumble the container prior to removing the sample to try and have a homogeneously distributed material to use or analyze. Carrying out several trials on the same material will also give confidence in the results, if similar results are seen from trial to trial.

MIXING THE COMPOSITIONS

Once all the powders are measured out, they can be added together into a suitable mixing bowl. A small brush is helpful to brush out any leftover powder that sticks to the weighing container (remembering to clean the brush afterwards to avoid cross-contamination to different mixtures). At this point, there are several techniques that can be used to dry-mix powders as needed. First, a stirring rod (such as one made of Teflon® or other smooth plastic) can be used to stir the powders together in the container. Alternatively, a pestle can be used to help break up chunks of powder that may not have loosened up (being careful not to grind powders too much, if a specific particle size is needed). Finally, if the composition is not expected to be impact- or friction-sensitive to ignition, the composition can be closed inside a container and shaken vigorously to mix up the solids. With any agitation of powders, one must understand the sensitivity nature of the composition, as unexpected ignition can occur in the right conditions.

The powder should be as intimately mixed as possible with whatever technique is used. And if several different compositions are to be compared, the *same technique should be used*: which includes the same type of equipment, same mixing style, and same mixing time. There is no way available to remove all discrepancies but staying as consistent as possible in mixing will help reduce as much variation as possible when it comes to analyzing differences in two or more compositions.

An advanced technique of some pyrotechnicians is to add the powders to a particle-size sieve, one whose mesh size is slightly larger than the particles in question, and use a brush to mix and push the powders through the screen. This not only helps to break up larger chunks but can provide pretty good mixing effectiveness (if the scientist doesn't mind, a little extra work). Figure 5.4 shows black powder being mixed on a mesh screen sieve, with the pyrotechnician's gloved hand helping mix and push the powder through the mesh.

Wet-mixing composition is another technique, whether using water or another medium such as organic solvents (acetone, alcohol, or others). Caution must always be used with organic solvent: their liquids and vapors can be quite flammable in air and can ignite any nearby pyrotechnic compositions. The wet slurry can be mixed and then dried fully before use.

Wet mixing also allows for granulation of mixed pyrotechnics before drying. Granulation is a valuable technique to avoid separation of solid powders during storage and transport, as well as to reduce dusting. With granulation, a wet slurry (often with a binder) is passed through a large-opening sieve to produce grains that are then dried before storage, transport, and use.

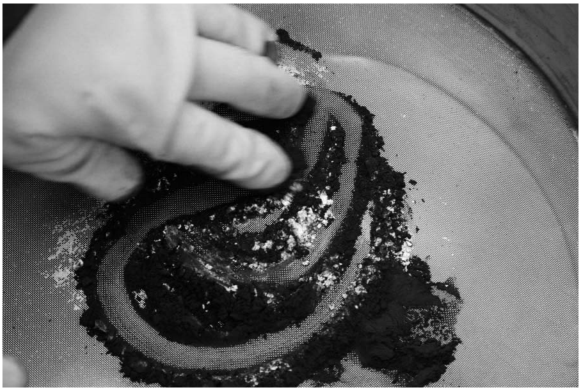

FIGURE 5.4 A gloved hand helps mix black powder components on a mesh screen, which will simultaneously push them through the holes in the screen. This technique is favored by some to help intimately mix powders as well as ensure the proper powder sizes that are desired. (Photo by Tim Wade and Dennis King, courtesy of MP Associates)

For all of these techniques, remote mixing and "barricading" of pyrotechnics is always an option for safety purposes. A rotating drum or tumbler can be turned on remotely, and then turned off remotely, to avoid nearby close contact hazards. A protective screen or shield can be placed around the mixing area as well.

In some cases, the compositions are meant to be pressed into specific forms, such as into pellets or into tubes (for whistle effects, see Chapter 12 on "Sound Production"). Special presses and pellet-making tools are used to assist in the production.

Once the composition is mixed, it is ready to go to the "firing range" for ignition.

USING THE LABORATORY HOOD "FIRING RANGE"

Setting Up the Lab Hood/Firing Range

Since we are working with small amount of material, a large military-style firing range (meant for large tests) is not necessary or even desirable. Instead, a proper laboratory fume hood or similar apparatus is used. Since flames and hot ash is created as part of pyrotechnics, the inside of the fume hood should be protected and set up in a way to preserve the hood and the safety of the scientist. For example, the inside of the fume hood should be lined completely with sheet metal—sides, bottom, and roof without blocking inside lighting—which can be replaced as needed. The front of lab hoods are often thick glass although adding another layer of thick plastic sheeting (such as Plexiglass®) is helpful as that can be replaced when burn marks become too prevalent.

In addition to protecting the fume hood, setting up a stand to ignite the materials on is also useful. Cinderblock or other flat-stone products are very helpful. A small "table" of cinderblocks can be constructed. Figure 5.5 shows a (working) pyrotechnic laboratory hood being used to ignite material on top of such a stand.

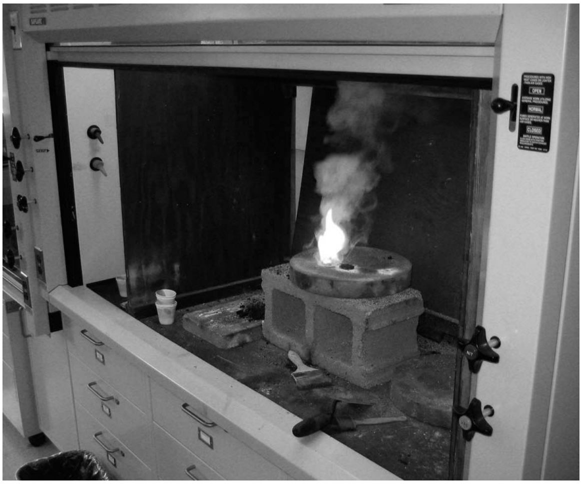

FIGURE 5.5 A working pyrotechnic "firing range" lab hood. Note that the fume hood has been lined with protective material (a wooden box with protective paint) to avoid burning the inside of the hood itself, and a cinderblock "table" has been constructed for easier ignition and viewing of the burning pyrotechnic.

IGNITING THE COMPOSITION

When the composition is ready, place a small pile of the mixed composition on the fireproof table, insert a selection of safety fuse into the base of the pile (at least 2–3 in. in length), and carefully light the end of the fuse with a match. Step back, close the fume hood if necessary, and observe the effect. Because of the generation of smoke by most pyrotechnic compositions, these tests are best conducted in a well-ventilated area such as a laboratory fume hood. Be certain no flammable materials are near the test area, for sparks may be produced. In the case of pressed pellets, these can sometimes "take flight" if gas generation is sufficient, leading to a very hot, burning solid flying around, or even out of, the hood. The hood window should always be closed when working with pressed pellets or larger single pieces of pyrotechnics. Be sure to keep a bucket of water or appropriate fire extinguisher handy, just in case.

If a bulk amount of material is mixed, but only a small portion is fired at one time, *never* pour from the bulk bottle onto the firing range table. Instead, use a scoop to transfer the powder, or pour the appropriate amount of powder into a transfer container and use that to pour the powder onto the firing table. The reason for this is that, if hot ash is leftover on the table, it can ignite powder that it comes into contact with, leading to a firing-train of reaction that leads right up to the main bottle and serious injury.

All testing of pyrotechnic compositions must be carried out under the direct supervision of a responsible adult well-trained in standard laboratory safety procedures. Serious injury can result from working with larger amounts of composition or from the misuse of pyrotechnic mixtures, so caution and adequate supervision are mandatory.

CLEANUP AND A FINAL NOTE ON SAFETY

Once the testing is done, leftover ash should be swept off from the burn surface (as some of it may not be completely reacted). At the end of the day, all ash should be left to cool down and swept up for disposal. One common practice is to try to "re-burn" the ash pile by using a propane igniter or Bunsen burner to try to ignite any remaining material. Once all ash is cooled down, it can be disposed of properly: sometimes in common municipal-waste trash, sometimes in specific solid waste containers if toxic chemicals (mercury, lead, chromium) are used but always in accordance with federal, state, and local laws and regulations.

A final word on mixing and firing: There is an unverified axiom among pyrotechnicians that for every one-million actions by the technician (opening a bottle is one action, weighing powder is one, mixing a composition is one, pouring it to the table is one, lighting a fuse is one, and so on) there will be an "accident" or unintended event. While there has been no way to verify this adage, every best precaution should be taken to minimize the risk that accidents—and they will happen with energetic materials—will cause serious harm or worse to people and property. Proper training and supervision is vital with pyrotechnics.

Now that a composition has been tested for its effect in a fume hood, let us look closer at analytical techniques that can be used to further investigate the properties of pyrotechnics and possibly help the scientist understand and improve their products.

ANALYSIS AND PYROTECHNICS

INTRODUCTION TO ANALYSIS OF PYROTECHNIC COMPOSITIONS

If a pyrotechnician tries out a new composition but does not receive the intended effect, there are two options for improving: *randomly* keep trying different chemicals and different combinations in hopes something works or, more logically, *analyze* the composition and its effects to render a hypothesis to be tested. Modern instrumental methods of analysis have provided scientists with a wealth of information regarding the nature of the solid state and the reactivity of solids. Knowledge of the structure of solids and an ability to study thermal behavior are essential to an understanding of the ignition behavior of high-energy materials. Modern technology has provided energetic materials scientists with the ability to analyze:

- Chemical makeup, including purity
- Ignition processes
- Sensitivity to ignition (see Chapter 7)
- Micro-structure of solids and mixture layouts
- Thermal (heat) and barometric (pressure) behavior and output
- Reaction products
- Quantification of visual (brightness and color) and auditory (loudness) effects
- Effects of external stimuli (environmental conditions and time) on chemicals and compositions

The vast sea of techniques and technologies available to modern scientists does not allow for all possible analytical methods and systems to be discussed here. However, this section will briefly discuss those tools and approaches that are common to energetic materials and pyrotechnics.

Instrumental analysis can be broken down into several divisions/techniques:

- Thermal analysis—changes with temperature/interaction with heat, probably the most important technique to a pyrotechnician
- Spectroscopy—analysis of light/electromagnetic radiation
- Spectrometry—analysis of mass-to-charge ratios
- Chromatography—separation of chemicals
- Microscopy—visualization of chemicals/analytes
- Crystallography—determination of crystal structure
- Electroanalysis—determination of electric potential/current

Let us look briefly at the techniques and instruments most common to pyrotechnic laboratories.

THERMAL ANALYSIS

Thermal analysis, or thermoanalysis, is the study of the thermal (heat) properties of a composition and is exceedingly valuable in pyrotechnics. This discipline studies the ignition temperature of a composition (or time-to-ignition), the burning temperature, the burning temperature over time, the total energy output (such as in calories or Joules), the energy output over time, the change in mass as compared to heat output (thermal gravimetry, or TG), and even analysis of the evolved gases (pyrolysis). We will cover an overview of useful techniques here and their application in subsequent chapters, however, the text *Introduction to Thermal Analysis* by M. E. Brown will provide further breadth and depth to this analytical system (Brown 1988).

Thermal Analysis using either differential thermal analysis (DTA) or differential scanning calorimetry (DSC) has provided a wealth of information regarding the thermal behavior of pure solids as well as solid mixtures (Gabbott 1998). DSC has emerged as the principal technique of thermal analysis over the past several decades—since it can provide enthalpy information where DTA cannot—although information obtained from either of the two methods is quite valuable. Melting points, boiling points, transitions from one crystalline form to another, and decomposition temperatures can be obtained for pure materials. Reaction temperatures can be determined via DSC for mixtures, such as ignition temperatures for pyrotechnic and explosive compositions.

DSC detects the absorption or release of heat by a sample as it is heated as a constant rate from room temperature to an upper limit, commonly 500°C (but can go higher). Any heat-absorbing changes occurring in the sample (e.g., melting or boiling) will be detected, as will processes that evolve heat (e.g., exothermic reactions). These changes are detected by continually comparing the temperature of the incident sample (in our case, the pyrotechnic) with that of a thermally inert reference material—often silicon dioxide or aluminum oxide—that undergoes no phase changes or reactions over the temperature range being studied. In the latter case, as the reference is heated, it will simply get hot without absorbing or releasing any extra heat. Both sample and reference are placed in contact with thermocouples[2] and heated at a constant rate. Current is applied to the electric heater to produce a linear temperature increase (typically 10°C–50°C/min) (McLain 1980). Figure 5.6 shows a mock-up drawing of a DTA.

If an endothermic (heat-absorbing) process occurs, the incident sample will momentarily become cooler than the reference material; in other words, heat is applied to the reference which gets hot, while the same heat is applied to the incident sample, which momentarily absorbs the heat *and does not get hotter*. The small temperature difference is detected by the pair of thermocouples and a deflection, termed an *endotherm*, is produced in the plot of T (temperature difference between sample and reference) versus T (temperature of the heating block). Evolution of heat by the sample will similarly produce a deflection in the opposite direction, termed an *exotherm*. For example, if black powder is heated, it will eventually ignite and be quite a bit hotter than the reference material at the same temperature input.

The printed output produced by the instrument, a *thermogram,* is a thermal "fingerprint" of the material being analyzed. Some representative thermograms of high-energy materials are shown in Figures 5.7–5.9, with more shown in later chapters.

Thermal analysis is quite useful for determining the purity of materials; this is accomplished by examining the location and "sharpness" of the melting point. DSC is also useful for qualitative identification of solid materials, by comparing the thermal pattern with those of known materials. Reaction temperatures, including the ignition temperatures of high-energy materials, can be quickly (and safely) measured by thermal analysis. These temperatures will correspond to conditions of rapid

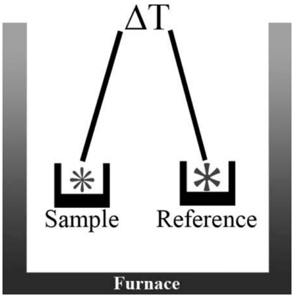

FIGURE 5.6 A mock-up drawing of a differential thermal analyzer, or DTA. Inside a furnace that will heat two materials, a sample holder to be analyzed and a reference sample both sit in containers with thermocouples placed inside of them. As the furnace heats, the thermocouples will record the temperature of both the sample as well as the reference. Any differences in temperature (ΔT) will be recorded by the DTA and placed on a plot, or "thermogram" as a function of overall temperature of the furnace.

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[2] Thermocouples are electrical connections that act as temperature sensors. Thermocouples change voltages based on their temperature; so, as a thermocouple gets hot, the voltage changes, and another electrical device reading that voltage can back-convert that into a temperature reading for the user.

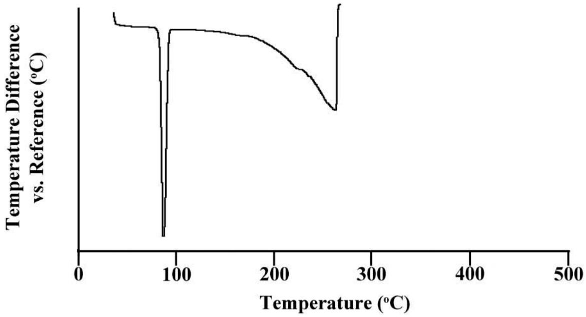

FIGURE 5.7 The differential scanning calorimetry (DSC) thermogram for pure 2,4,6-trinitrotoluene (TNT). The major features are an endotherm corresponding to melting at 81°C and an exothermic decomposition peak beginning near 280°C (the apparent endotherm beginning after 200°C is from the thermocouple probe being moved out of the sample and into the air, making it look as though the sample is cooler than it actually is). The *x*-axis represents the temperature of the heating block in degrees centigrade. The *y*-axis indicates the difference in temperature, Δ*T*, between the sample and an identically heated reference solid, typically glass beads or aluminum oxide: The reference solid only gets hot in line with the warming heating block, while the pyrotechnic composition will be cooler than the reference if melting or undergoing another endothermic change and will be hotter than the reference upon combustion.

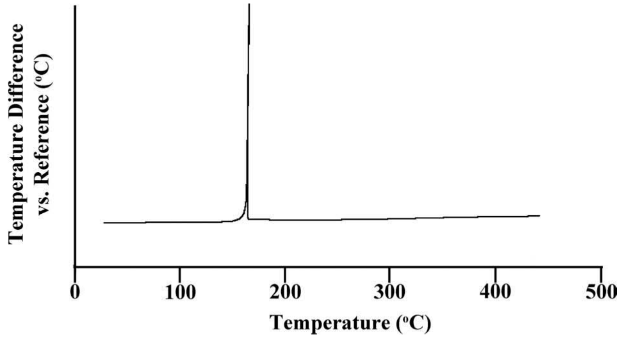

FIGURE 5.8 The differential scanning calorimetry (DSC) thermogram for pure nitrocellulose. The major feature is an exotherm corresponding to melting and subsequent decomposition and ignition near 160°C–170°C.

heating of a confined sample and must be recognized as such. A variety of other types of analysis, such as accelerated aging, can also be performed with thermal analysis technology (Gabbott 1998).

Our understanding of the ignition phenomenon has been greatly enhanced using thermal analysis to examine energetic mixtures. Analysis of the thermograms of numerous pyrotechnic mixtures has indicated that the thermal activation of one or more of the components of the mixture is required for ignition to occur. Mobility—the ability for one component to intimately mix with another—is important; furthermore, the oxidizer and fuel must be in intimate contact for a rapid reaction to ensue.

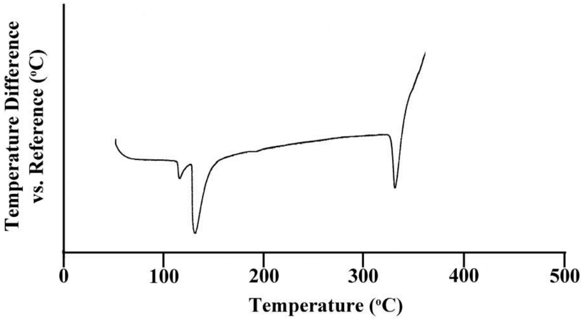

FIGURE 5.9 Black powder was the first "modern" high-energy mixture and it is still used in a variety of pyrotechnic applications. It is an intimate blend of potassium nitrate (75%), charcoal (15%), and sulfur (10%). The thermogram for the mixture shows an endotherm between 105°C and 119°C, corresponding to a solid–solid phase transition and melting for sulfur (two endotherms overlap into one), a strong endotherm near 130°C representing a solid–solid transition in potassium nitrate and a final strong endotherm near 330°C representing potassium nitrate melting followed immediately by a violent exotherm where ignition of the mixture occurs.

Melting, boiling, and decomposition temperatures are therefore quite important to the ignition process. Melting exposes fresh, reactive surfaces and creates the fluid, liquid state. Intimate mixing is facilitated by melting, while vaporization allows mixing to occur at an even faster rate. We will return to this topic in Chapter 6 and also discuss time-to-ignition studies (where a constant temperature is applied to a mixture and the time for the material to ignite is recorded).

Another useful technique, thermal gravimetry (TG), monitors the weight of a sample on heating and can detect temperatures where samples lose weight through evaporation or gas evolution or gain weight through air oxidation (Brown 1988). Interestingly, when gases are evolved in such studies, they can be directly fed into a mass spectrometer or infrared spectrophotometer so that their chemical identities can be determined to provide additional information about a material's behavior upon heating.

The advantages of using thermal analysis to study energetic materials begin with the fact that very small sample sizes (1 mg or less) can be studied. If a material should ignite upon heating during a run, there should be little or no damage to the instrument (although sometimes thermocouples do need to be replaced after witnessing significant deflagrations). In addition, no pretreatment of the sample is typically required—it can be a powder, a slurry, a particle, or a granule.

Some applications of thermal analysis instrumentation in energetic materials include the following:

1. The qualitative identification of materials and components in mixtures by solid–solid phase transition temperatures and melting points
2. Purity determination of chemicals (quality control) by the location and sharpness of melting points determined by the use of a DSC
3. Investigation of the ignition process for energetic mixtures—comparison of the ignition temperature to phase transitions and decomposition temperatures in the components

4. The coupling of DSC with thermogravimetric methods to compare data by the two methods and correlate peaks in the DSC thermogram with weight gain or weight loss by TG. Gas output in TG studies can also be analyzed by other analytical methods (mass spectrometry or infrared spectroscopy) to identify gases that are evolved in the TG study.

HEAT OUTPUT MEASUREMENT

A bomb calorimeter is the standard device used for the measurement of the heat output, upon ignition, of an energetic mixture. A weighed sample is ignited, usually with a bit of hot wire, and the temperature rise is measured. Knowing the heat capacity of the instrument, the temperature rise can be converted into heat output. Current calorimeters on the market offer a range of options, including automated data processing and data storage.

This equipment can be used for research work with new compositions, to compare expected heat output with experimental. It can also be used for quality control work—new each batch of "identical" energetic material that is manufactured, or perhaps is purchased from another manufacturer, should produce the same heat output per gram as the "standard" material. If it does not, the reason needs to be determined before the new material is put into production. Also, a calibrated DSC can be used to determine the heats of various processes that occur in energetic materials as the sample temperature is raised.

SPECTROSCOPY

Coming from the term "spectro" indicating light and the Greek term "skopia" for "watching," spectroscopy—watching light—is the study of the dispersion of light (which is electromagnetic radiation) and its interaction with matter. Spectroscopy will not only measure the intensity of these radiation waves but also their energy and wavelengths. As we learned in Chapter 2, the human eye perceives certain wavelengths as color, and we will explore this concept further as it pertains to pyrotechnics in Chapter 10. When pyrotechnics emit light and color, the total intensity can be quantified with a photometer, and the individual wavelengths can be quantified very accurately by a spectrometer/spectrophotometer (see Figure 4.1).

Some other useful spectroscopic techniques include Fourier transform infrared spectroscopy, FTIR, which analyzes the wavelengths of infrared light that are absorbed by molecules (based on movement of their molecular structure) and outputs a "spectrum" that can be indicative of the specific or class of chemical(s) present. X-ray fluorescence induces x-rays upon a material, causing it to "fluoresce" or emit light in a particular pattern that can be a fingerprint for the chemical present. Raman spectroscopy is the analysis of scattered light from a chemical after intense light interacts with the molecules, which is also useful for the "fingerprint" identification of chemicals. So-called "UV–Vis" spectroscopy is the analysis of ultraviolet and visible color wavelengths, sometimes for quality control and very much applicable in the world of colored dyes used in pyrotechnics.

MICROSCOPY

Microscopy, or “looking small,” is the use of special lenses and equipment to enhance visualization of materials and features that are not visible to the naked eye. Pyrotechnicians will most often use “optical” microscopy, using visible light, although other advanced techniques (such scanning electron microscopy, scanning-tunneling microscopy, and atomic force microscopy) are useful practices in other scientific disciplines. With solid materials, microscopy can help show the size of particles, their morphology (sphere, granule, flake, etc.), and how well materials are mixed. For quality control, microscopy is critical to understanding any differences from one batch to the next of the same chemical and should be a part of normal QC practices upon receiving new batches of chemicals.

MOISTURE ANALYZER

If there is one thing that can cause significant variation from batch-to-batch in the production of energetic mixtures, it is water. Water is a tremendous heat sink and slows the burn rate of most energetic mixtures. It is also a reactive chemical and can react over time with magnesium, zinc, and other metal fuels, leading to a slowing of the burn rate for the mixtures containing these fuels. It can also change the particle size of water-soluble components over time, as a material goes through thermal cycling. Some of the water-soluble particles dissolve at higher temperatures and then recrystallize back out as the material cools—with a possible change in particle size. This can affect your burn rate as well. Therefore, you need to know the moisture content of pyrotechnic mixtures when they are ready to be loaded into end items.

The equipment for this analysis can be as simple as an oven and a sensitive electronic balance. Weigh the sample before and after heating in the oven, using a temperature warm enough to remove moisture from the sample but low enough to minimize the possibility of an ignition. Obviously, small samples are desirable for this study.

OTHER EQUIPMENT AND TECHNIQUES

Depending on the specific types of energetic material that is produced at a given facility, other equipment should be on hand for quality control work, as well as research and development work. This could include light and color analysis for illuminant and flare compositions, as noted earlier, and light obscuration equipment for obscuration (smoke) production.

Two techniques common among “benchtop chemists” are chromatography (the separation of chemicals) and mass spectrometry (determining the mass of charged ions from that of the chemical identity). This tandem system—sometimes in the form of gas chromatography/mass spectrometry or GS/MS—is an extremely powerful tool in determining the constituents of a mix of chemicals. A pyrotechnician could use this not only for quality control of chemicals but also to understand the nature of leftover residues or changes in materials after storage over time.

X-ray crystallography has provided the crystal type and lattice dimensions for numerous solids. In this technique, high-energy x-rays strike the crystal and are diffracted in a pattern characteristic of the particular lattice type. Complex mathematical analysis can convert the diffraction pattern to the actual crystal structure. Advances in computer technology have revolutionized this field in the past few years. Complex structures, formerly requiring months or years to determine, can now be analyzed over a very short duration. Even huge protein and nucleic acid chains can be worked out by the crystallographer (Moore 1983).

Sound analysis with a sound or decibel meter is important when the noise output of a pyrotechnic is important (such as flash-bang compositions for law enforcement or military applications). Digital particle size analyzers can assist in determining the average particle size of bulk powders, sometimes to an even more accurate degree than the sieve method discussed earlier. Gas volume analyzers/pressure measurement equipment are, naturally, useful for propellant analysis. These can include pressure rate-of-rise measurements as well for generation over time.

There are numerous pieces of equipment used for studying and analyzing the sensitivity of pyrotechnics to external stimuli for ignition—not just heat but also friction, spark, impact, and shockwave—and those will be discussed in detail in Chapter 7.

PROCESS HAZARD ANALYSIS

An important feature of the manufacturing and analysis of all energetic materials today is the use of hazard analysis methodology for all operations involving the presence of exposed energetic materials. A team, including personnel working in the area of the process under review, technically trained individuals, and persons familiar with hazard analysis methodology review each operation. First, the current Standard Operating Procedures are examined, along with information such as MSDSs (for Material Safety Data Sheet), equipment specifications, sensitivity data, and past incidents involving the process. Then the team reviews the process, looking for possible things that might go wrong and lead to an incident. Corrective actions, if required, are recommended and implemented as necessary. If any "change" occurs in a given process, a new hazard analysis in conducted to determine if the "change" requires any modifications to the hazard analysis plan for the operation, such as new or revised standard operating procedures.

LABORATORIES AND ANALYSIS: A FINAL NOTE

A safe, properly stocked, and analytically capable pyrotechnic laboratory is essential for any scientist who is attempting to advance the science and understanding of pyrotechnics, including preparing new formulas and compositions for exploration. A world of tools and techniques are available to help the investigator understand their work, as well as provide them information to help them improve it. However, *safety* and *proper technique* are always the most important tools in the pyrotechnician's toolbox.

And, as always: keep your powder dry.

6 Ignition and Propagation

BURNING NITROCELLULOSE: Nitrocellulose, produced by the reaction of nitric acid with cellulose, provided the first new propellant material since the development of black powder. Introduced in the late 19th century, this material served as the primary ingredient for "smokeless powders" that revolutionized the propellant industry. Nitroglycerine, another energetic material developed in the 19th century, was combined with nitrocellulose to make other smokeless propellants, as well as used by itself to make Alfred Nobel's "dynamite", which revolutionized the blasting industry.

Now with the understanding of the material chemicals and technical principles involved in pyrotechnics, we are ready to study them in action. At the start of any pyrotechnic event is *ignition*, which must be followed by *propagation* (continuation) of burning for any pyrotechnic to be of any technical use. Concurrently, for an energetic material to be of any practical use, the pyrotechnician must be able to not only prepare it safely and reliably but must also be able to ignite it safely and reliably—ideally using something less dramatic than prolonged exposure to an acetylene blowtorch at 3,000^{o} Celsius! One of the best analogies to use with ignition and propagation is starting a warm wood fire in the fireplace on a cold winter day. Wet wood is difficult to light, small slivers of wood ignite more readily than a large diameter log, and no additional crumpled newspaper is required once the wood fire is under way.

INTRODUCTION TO IGNITION PRINCIPLES

A pyrotechnic composition must be capable of undergoing reliable ignition when an ignition stimulus is provided and yet be stable in transportation and storage against undesired ignition. A tricky balance! The ignition behavior of every mixture must be studied so the proper ignition system can then be specified for use with each composition. For easily ignited materials, the "spit" from a burning black powder fuse is often sufficient. The ignition method for propellants is frequently an impact-sensitive energetic "primer" that produces a spray of hot particulates and a flame to rapidly get the propellant burning. Another common igniter is an electric match, sometimes called a "squib," consisting of a wire circuit terminating in a small-diameter hot bridge wire, or just "bridgewire," that is coated with a small dab of heat-sensitive composition. An electric current is passed through the circuit, producing sufficient heat to ignite the bridgewire composition and produce a flame. The burst of flame then ignites the next composition in the ignition sequence. For pyrotechnic mixtures with high-ignition temperatures, a priming composition or "first fire" is often used. This is an easily ignited composition that can be reliably activated by a fuse or other igniter. The flame and hot particulates that are produced are then used to ignite the main composition.

Successful performance of a high-energy mixture depends upon:

1. Ignition—The ability to *ignite* the material using an external stimulus, as well as the *stability* of the composition in the absence of the stimulus.
2. Propagation—The ability of the mixture, once ignited, to sustain, or *propagate* burning through the remainder of the composition.

These two processes (ignition and propagation) logically share a number of common factors, but there are also some differences related to the involvement of *external* versus *internal* energy. An ideal composition will readily ignite only when desired, then continue to burn reliably to produce the desired effect ordered by the customer, all produced at an acceptable cost and all while remaining quite stable during manufacture and storage. This is not an easy set of requirements to meet and is one of the main reasons why a relatively small number of materials are used in preparing high-energy mixtures.

IGNITION TECHNIQUES

Ignition of an energetic material can be achieved using a variety of types of energy input. Traditional methods such as flame, hot particles/sparks, impact, and friction continue to be used to initiate devices. Flame and spark will obviously transfer their heat to the "cooler" pyrotechnic material to ignite the material. But recalling the first law of thermodynamics—energy is neither created nor destroyed, only transferred—the energy from impact and friction[1] can be transferred as heat to unreacted material, igniting the composition.

Ignition using electric current or electric spark has been the "state-of-the-art" for ignition of many types of energetic materials for decades. Newer methods to create a "hot spot," such as the use of electromagnetic radiation ("light"), fiber optics, and laser technology, are all being further developed and used to address specific concerns with electrical ignition that involves possible unintended ignition due to electrostatic discharge and stray radiofrequency (RF) signals that could inadvertently ignite bridgewire-type systems (De Yong and Lu 1998).

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[1] One needs to only run their hands together on a cold day to understand how friction can generate heat.

IGNITION: INITIAL AND CONTINUING EVENTS

Application of the ignition stimulus (such as a spark or flame) initiates a complex sequence of events in the chemical composition, if the externally applied energy is effectively absorbed by the energetic material. The solid components may undergo crystalline phase transitions, melting, boiling, and/or decomposition. Liquid and vapor phases may be formed, and a chemical reaction will eventually occur at the surface where the energy input is applied, *if the necessary activation energy* has been provided via a temperature rise in a portion of the material receiving the external energy.

The heat released by the occurrence of the high-energy reaction raises the temperature of the next layer or grain of composition. If the heat evolution and thermal conductivity are sufficient to supply the required activation energy (via a temperature increase) to the next layer, further reaction will occur, liberating additional heat, and propagation of the reaction through the mixture will take place. The rates and quantity of heat transfer *to*, heat production *in*, and heat loss *from* the high-energy composition are all critical factors in achieving propagation of burning via a self-sustaining chemical reaction. To put it another way, a first section of material must accept heat and burn, must liberate sufficient heat from its own burning, and then must transfer sufficient heat to a second section without unnecessary loss to the surroundings, which then must accept the heat and burn, etc.

The combustion process itself is quite complex, involving high temperatures and a variety of short-lived, high-energy chemical species. The solid, liquid, and vapor states may all be present in the actual flame (in addition to the fourth state, plasma), as well as in the region immediately adjacent to it. *Products* will be formed as the reaction proceeds, and they will either escape as gaseous species or accumulate as solids in the reaction zone, as shown in Figure 6.1.

COMBUSTION, DEFLAGRATION, AND DETONATION

A moving, high-temperature reaction zone, progressing through the composition, is characteristic of a combustion (or "burning") reaction. This zone separates unreacted starting material from the reaction products. A high-temperature zone of this type is *not* found in "normal" chemical reactions, such as those carried out in a flask or beaker, where the entire system is at the same temperature and molecules react randomly throughout the container. Combustion and deflagration (which is a *very* rapid combustion) are distinguished from detonation by the absence of a significant pressure differential between the region undergoing reaction and the remainder of the unreacted composition (Shidlovskiy 1964). In deflagration, the material is combusting at a rate that appears to be nearly instantaneous, which may seem like a detonation. However, the same process of combustion applies in deflagration: The heat released from the reacted material is transferred to the unreacted material, which initiates burning, propagating the overall reaction. In other words, *heat transfer* propagates a deflagration.

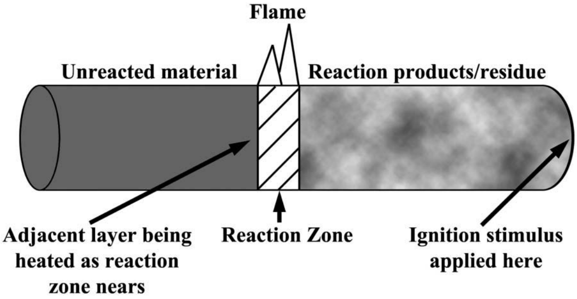
Flame
Unreacted material
Reaction products/residue
Adjacent layer being heated as reaction zone nears
Reaction Zone
Ignition stimulus applied here

FIGURE 6.1 Burning pyrotechnic composition. Several major regions are present in a reacting pyrotechnic composition. The actual self-propagating exothermic process is occurring in the reaction zone. High temperature, flame and smoke production, and the likely presence of gaseous and liquid materials characterize this region. Behind the advancing reaction zone are solid products formed during the reaction (unless all products were gaseous). Immediately ahead of the reaction zone is the next layer of composition that will undergo reaction. This layer is being heated by the approaching reaction, and melting, solid–solid phase transitions, and low-velocity pre-ignition reactions may be occurring. The thermal conductivity of the composition is quite important in transferring heat from the reaction zone to the adjacent, unreacted material. Hot gases as well as hot solid and liquid particles aid in the propagation of burning.

In contrast, a detonation creates an extremely high-pressure zone, as compared to unreacted material, that deflagration does not generate in the same extreme. This high-pressure zone moves as a wave through the unreacted material at over a kilometer per second, forcing unreacted material to compress and rapidly heat up due to the pressure, resulting in their decomposition into highly reactive pieces (Akhavan 2004). In other words, a detonation wave effectively "shatters" molecules, leaving molecular and atomic fragments following the shock front. The fragments will recombine, releasing energy that sustains the shockwave moving through the remaining unreacted material. In detonation, it is *shockwave speed* that propagates the detonation.

So, to compare, in deflagration, the speed of the overall reaction is dictated by how fast the heat-transfer process takes place, while in detonation, the speed of the overall reaction is dictated by a supersonic compression wave. It goes without saying, heat transfer is relatively slow, supersonic pressure waves are relatively fast, and detonations are much more instantaneously energetic.

IGNITION FACTORS: PART 1

For ignition to occur, a portion of the mixture must be heated to its *ignition temperature*, which is defined as the minimum temperature required for the initiation of an immediate, rapid, self-propagating exothermic reaction. Upon ignition, the reaction then proceeds on its own—or *propagates*—through the remainder of the energetic mixture and in the absence of any additional external energy input (i.e., not requiring the pyrotechnician to hold a blowtorch to the material to maintain burning). A variety of factors affect the ignition temperature and the burning rate of a high-energy mixture, and the chemist has the ability to alter most of these factors to achieve a desired change in performance.

One requirement for ignition appears to be the need for either the oxidizer or fuel to be in the liquid (or sometimes vapor) state, and reactivity becomes even more certain when both the fuel and oxidizer are liquids or gases. The presence of a low-melting fuel can substantially lower the ignition temperature of many compositions (Barton 1982). This is particularly true when the melting of a fuel is accompanied by thermal decomposition of the material, generating readily oxidizable fragments. Sulfur and organic compounds have been employed numerous times as "tinders" in high-energy mixtures to facilitate ignition. Sulfur melts at 119°C, while most sugars, gums, starches, and other organic polymers have melting points or decomposition temperatures of 300°C or less. This property can be used to lower the ignition temperature, sometimes drastically, of other mixtures by adding an amount of low-melting/decomposing sulfur or organics, as shown in Table 6.1. The presence of this newly formed "fluid" state in the composition helps provide for the first requirement for ignition: intimate mixing of oxidizer and fuel. There is of course still an energy requirement—the activation energy—that must be overcome, however, in order to achieve ignition. This activation energy relates to the decomposition of the oxidizer, resulting in the *release* of oxygen, as well as the activation or decomposition of the fuel to be able to *accept* the oxygen and form reaction products, releasing heat.

TABLE 6.1
Effect of Sulfur and Organic Fuels on Ignition Temperature

	Composition	% by weight	Ignition Temperature (°C)
IA.	$KClO_4$	66.7	446[a]
	Al	33.3	
IB.	$KClO_4$	64	360
	Al	22.5	
	S	10	
	Sb_2S_3	3.5	
IIA.	$BaCrO_4$	90	615[a] (3.1 mL/g of evolved gas)
	B	10	
IIB.	$BaCrO_4$	90	560 (29.5 mL/g of evolved gas)
	B	10	
	Vinyl alcohol/acetate resin	+1%	
IIIA.	$NaNO_3$	50	772[b] (50 mg sample, heated at 50°C/min.)
	Ti	50	
IIIB.	$NaNO_3$	50	357
	Ti	50	
	Boiled linseed oil	+6%	

[a] McIntyre (1980).

[b] Barton (1982).

LATTICE STRUCTURE, MOTION, REACTIVITY, AND "THE TAMMANN TEMPERATURE"

Many of the oxidizers used in high-energy mixtures, such as potassium nitrate, are ionic solids, and the "looseness" of the ionic lattice is quite important in determining their reactivity (McLain 1980). A crystalline lattice has some vibrational motion at normal room temperature,[2] and the amplitude of this vibration increases as the temperature of the solid is raised. At the melting point, the forces holding the crystalline solid together collapse, producing the randomly oriented liquid state. For reaction to occur in a high-energy system, the fuel and oxygen-rich oxidizer anion must become intimately mixed on the ionic or molecular level. Liquid fuel or fuel fragments can diffuse into the solid oxidizer lattice *if* the vibrational amplitude in the crystal is sufficient. Once sufficient heat is generated to begin decomposing the oxidizer, the higher temperature combustion reaction begins, involving free oxygen gas and fuel atoms or radicals, and very rapid reaction rates can result. We are concerned here with the processes that *initiate* the ignition step.

Professor Gustav Andreas Tammann, one of the pioneers of solid-state chemistry, considered the importance of the lattice motion to reactivity and used the ratio of the actual temperature of a solid divided by the melting point of the solid (with all temperatures expressed in the Kelvin or "absolute" scale) to quantify this concept. Where the Tammann temperature is calculated:

$$T_{\text{Tammann}} = \text{Temperature}(\text{solid})/\text{Temperature}(\text{melting point})(\text{in K}) \tag{6.1}$$

Tammann proposed that diffusion of a mobile species into a crystalline lattice should be "significant" at a value of 0.5 (or halfway to the melting point, on the Kelvin scale). For example, the melting point of potassium nitrate is 334°C, or 334+273=607 Kelvin. Take half of this value (303.5 K), and then subtract 273 to convert back to the Celsius scale, giving a value of 30.5°C (or 93°F)—a temperature likely to be found in a warm storage area.

At this temperature, later termed the *Tammann Temperature*, a solid has approximately 70% of the vibrational freedom present at the melting point, and diffusion into the lattice becomes probable (McLain 1980). If this represents the approximate temperature where diffusion becomes probable, it is therefore also a temperature where a chemical reaction between a good oxidizer and a mobile, reactive fuel becomes possible. Oxidizers begin to release oxygen at slow rates at temperatures below their melting points, and the rate of oxygen loss tends to become quite significant for many oxidizers as the melting point is reached. This is a very important factor from a safety standpoint: The potential for a reaction may exist at surprisingly low temperatures, especially with sulfur or organic fuels present. Table 6.2 lists the Tammann temperatures of some of the common oxidizers. The *low* temperatures shown for potassium chlorate and potassium nitrate may well account for the large number of mysterious, accidental ignitions that have occurred with fuel–oxidizer compositions containing these materials. Potassium chlorate is particularly vulnerable to this phenomenon, since the decomposition of the oxidizer is an *exothermic* process (See Table 3.2) that actually contributes energy to help get the ignition process underway.

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[2] All molecules are constantly vibrating, based on factors and complex systems such that whole books are written in attempt to explain them.

TABLE 6.2
Tammann Temperatures of the Common Oxidizers (and Magnesium)

Oxidizer	Formula	Melting Point (°C)	Melting Point (K)	Tammann Temperature (°C)
Sodium nitrate	$NaNO_3$	307	580	17
Potassium nitrate	KNO_3	334	607	31
Potassium chlorate	$KClO_3$	356	629	42
Strontium nitrate	$Sr(NO_3)_2$	570	843	149
Barium nitrate	$Ba(NO_3)_2$	592	865	160
Potassium perchlorate	$KClO_4$	610	883	168
Lead chromate	$PbCrO_4$	844	1,117	286
Iron oxide	Fe_2O_3	1,565	1,838	646
Magnesium metal	Mg	651	924	189

The significantly *endothermic* decomposition of potassium nitrate requires that a higher temperature be reached before decomposition commences, and oxygen is released at a significant rate for reaction with a waiting fuel species.

Tammann temperature indicates the temperature where mobility is possible, or even probable, in a solid oxidizer material. The other requirement for a binary pyrotechnic reaction, of course, is the presence of a reactive fuel or fuel fragment to accept oxygen from the oxidizer, thereby generating additional energy to lead to ignition. Adequate mobility and adequate energetics are both required for ignition to occur. The same logic applies to oxygen atoms from an oxidizer diffusing into a high-melting solid fuel and reacting with surface fuel atoms to generate heat.

IGNITION FACTORS: PART 2

Ease of ignition also depends on the particle size and surface area of the ingredients. This factor is especially important for metallic fuels with melting points higher than or comparable to that of the oxidizer. Some metals—including aluminum, magnesium, titanium, and zirconium—can be quite hazardous when present in fine particle size (in the 1–5 μm range), not to mention particles in the nanometer range. Particles this fine may spontaneously ignite in air and are often quite sensitive to static discharge (Ellern 1968). For safety reasons, reactivity is usually sacrificed to some extent when metal powders are part of a mixture, and ultrafine particle sizes are avoided to minimize accidental ignition.

A final requirement for ignition appears to be for the fuel to have reached a temperature where it has been activated toward oxidation. For metallic fuels, this usually involves the shedding of a surface oxide coating, exposing fresh metal atoms to the oxygen that is released from the oxidizer. This process tends to become significant when the temperature of the metal is well above its Tammann temperature and is approaching its melting point, and numerous oxidizer/metal fuel systems show ignition temperatures that coincide with the onset of melting of the fuel. For magnesium/oxidizer systems, as an example, ignition temperatures in the 600°C–650°C range are commonly observed (See Table 6.3).

TABLE 6.3
Ignition Temperatures of Magnesium-Containing Mixtures[a]

Oxidizer	Ignition Temperature (°C)
$NaNO_3$	635
$Ba(NO_3)_2$	615
$Sr(NO_3)_2$	610
KNO_3	650
$KClO_4$	715

Note: All mixtures contain 50% magnesium by weight. Loading pressure was 10,000 psi.

[a] Ellern (1968).

For organic fuels, the activation process appears to involve the fuel reaching a temperature where decomposition of the carbon chain commences, generating "free radical" fragments that are susceptible to oxidation. Organic compounds typically reach their decomposition temperatures from 200°C–350°C, depending on the particular molecular structure of the fuel. Many sugars, such as glucose and sucrose, have low decomposition temperatures (the familiar "caramelization" reaction that causes sugars to turn brown on heating), while hydrocarbon chains without electronegative substituents (such as halogens or nitro groups) tend to be more thermally stable. The presence of oxygen atoms on each carbon atom in a sugar molecule leads to considerable internal bond strain, as each carbon in the chain is rendered partially positive due to the presence of the attached, electronegative oxygen atom. The adjacent, partially positive carbon atoms tend to repel each other, leading to molecular instability at relatively low temperature. This same phenomenon is also responsible for the sensitizing of some molecular explosives, such as nitroglycerine, where the presence of electronegative atoms on adjacent carbon atoms destabilizes the molecule and renders the material shock- and impact-sensitive. Sulfur's tendency to act as a "tinder," or ignition aid, when present in pyrotechnic compositions can be traced to a low melting point that leads to activation toward oxidation.

Several examples will be given to illustrate these principles. In the potassium nitrate/sulfur system, the liquid state initially appears during heating with the melting of sulfur at 119°C. Sulfur occurs in nature as an 8-member ring—the S_8 molecule. This ring begins to fragment into species such as S_3 at temperatures above 140°C. However, even with these fragments present, reaction between sulfur and the solid does not occur at a rate sufficient to produce ignition until the KNO_3 melts at 334°C and oxygen evolution increases. Intimate mixing can occur when both species are in the liquid state, and ignition is observed just above the KNO_3 melting point. Although some reaction (a pre-ignition reaction, or PIR) presumably occurs between sulfur and solid KNO_3 below the melting point, the low heat output obtained from the oxidation of sulfur combined with the *endothermic* decomposition of KNO_3 prevent ignition from taking place until the entire system is liquid. Only then is the reaction rate great enough to produce a self-propagating reaction. Figures 6.2–6.4 show the thermograms of the individual components and then the mixture. Note the strong exotherm (release of heat) corresponding to ignition for the KNO_3/S mixture just above 330°C.

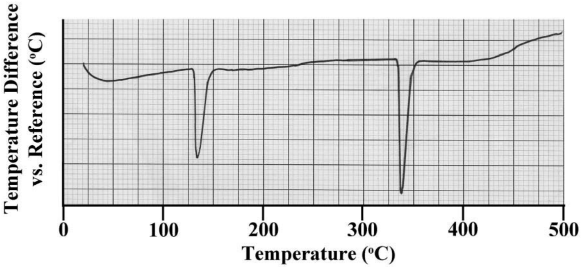


FIGURE 6.2 Thermogram of pure potassium nitrate. Endotherm is observed near 130°C and 334°C. These peaks correspond to a rhombic-to-trigonal crystalline transition and melting, respectively. Note the sharpness of the melting point endotherm near 334°C. Pure compounds will normally melt over a very narrow range. Impure compounds will have a broad melting point endotherm.

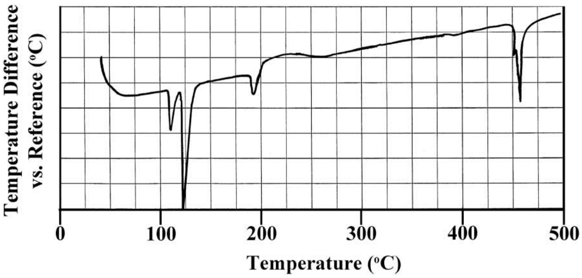


FIGURE 6.3 A sulfur thermogram. Endotherms for a rhombic-to-monoclinic crystalline phase transition and melting are seen at 105°C and 119°C, respectively. An additional endotherm is observed near 180°C. This peak corresponds to the fragmentation of liquid S_8 molecules into smaller units. Finally, vaporization is observed near 450°C.

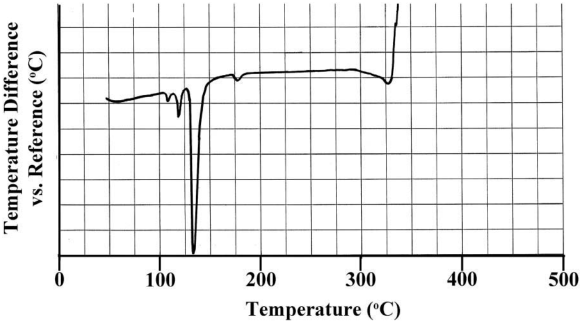


FIGURE 6.4 The potassium nitrate/sulfur/aluminum system. Endotherms for sulfur can be seen near 105°C and 119°C, followed by the potassium nitrate phase transition near 130°C. As the melting point of potassium nitrate is approached (334°C), an exotherm is observed. A reaction has occurred between the oxidizer and fuel, and ignition of the mixture evolves a substantial amount of heat.

In the potassium chlorate/sulfur system, $KClO_3/S$, a different result is observed. Sulfur again melts at 119°C and begins to fragment above 140°C, but a strong exotherm corresponding to ignition of the composition is found well below 200°C. Potassium chlorate has a melting point of 356°C, so ignition is taking place well below the melting point of the oxidizer. We recall, though, that $KClO_3$ has a Tammann temperature of 42°C. A mobile species—such as liquid, fragmented sulfur—can penetrate the lattice well below the melting point and be in a position to react. We also recall that the thermal decomposition of $KClO_3$ is *exothermic* (10.6kcal of heat is evolved per mole of oxidizer that decomposes). A compounding of heat evolution is obtained: heat is released by the $KClO_3/S$ reaction *and* by decomposition of additional $KClO_3$, generating oxygen to react with additional sulfur. More heat is generated and an Arrhenius-type rate acceleration occurs, leading to ignition well below the melting point of the oxidizer. This combination of low Tammann temperature and exothermic decomposition helps account for the dangerous and unpredictable nature of potassium chlorate. Figures 6.3, 6.5, and 6.6 show the thermal behaviors of the individual components and then the $KClO_3/S$ mixture. Similarly, ignition of the potassium chlorate/sucrose system is observed near 190°C, the melting and decomposition temperature of sucrose.

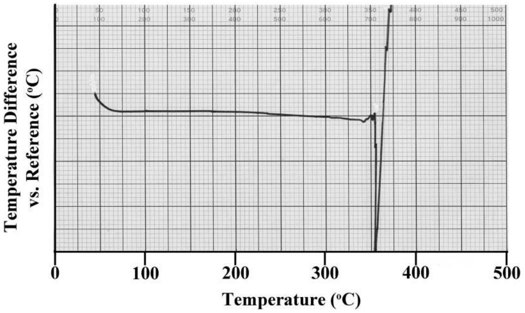


FIGURE 6.5 Thermogram of pure potassium chlorate, $KClO_3$. No thermal events are observed prior to the melting point (356°C). Exothermic decomposition occurs above the melting point as oxygen gas is liberated along with heat.

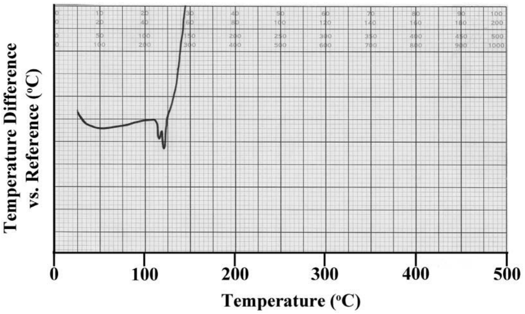


FIGURE 6.6 The potassium chlorate/sulfur system. Sulfur endotherms are seen near 105°C and 119°C, as expected. A violent exothermic reaction is observed below 150°C. The ignition temperature is approximately 200° below the melting point of the oxidizer ($KClO_3$m.p.=356°C). Ignition occurs near the temperature at which S_8 molecules fragment into smaller parts.

IGNITION TEMPERATURES

As we proceed to higher melting fuels and oxidizers, we see a corresponding increase in the ignition temperatures of two-component mixtures containing these materials. The lowest ignition temperatures, logically, are associated with combinations of low-melting fuels and low-melting oxidizers, while high-melting combinations generally display higher ignition temperatures. Table 6.4 gives some examples of this principle.

Table 6.4 also shows that several potassium nitrate mixtures with low-melting, readily decomposed fuels have ignition temperatures near or slightly above the 334°C melting point of the oxidizer. Mixtures of KNO_3 with higher-melting metal fuels (often metals) show substantially higher ignition temperatures. As noted previously, Table 6.3 shows that a variety of magnesium-containing compositions have ignition temperatures close to the 649°C melting point of the metal, where the magnesium oxide coating

TABLE 6.4
Ignition Temperature of Pyrotechnic Mixtures

Component		Melting Point (°C)	Ignition Temperature (°C)
I.	$KClO_3$	356	150
	S	119	
II.	$KClO_3$	256	195[a]
	Lactose	202	
III.	$KClO_3$	356	540[a]
	Mg	649	
IV.	KNO_3	334	390[a]
	Lactose	202	
V.	KNO_3	334	340
	S	119	
VI.	KNO_3	334	565[a]
	Mg	649	
VII.	$BaCrO_4$ (90)	Decomposes at high temp.	685[b]
	B (10)	2,300	
VIII.	Chinese firecracker		150
	($KClO_3$, S, Al)		
IX.	$KClO_3$	356	200
	Sugar	186	
X.	Black powder		340
	(KNO_3, S, charcoal)		

(*Continued*)

TABLE 6.4 (*Continued*)
Ignition Temperature of Pyrotechnic Mixtures

Component		Melting Point (°C)	Ignition Temperature (°C)
XI.	Flash powder ($KClO_4$, S, Al)		450
XII.	Gold sparkler ($Ba(NO_3)_2$, Al, dextrine, iron filings)		>500

Ignition temperatures determined by differential thermal analysis are presented above. These values represent the temperature at which a strong exothermic reaction appears in the thermogram of the mixture. An audible effect can be heard during many of these trials, indicating a violent reaction. Mixtures were in stoichiometric proportions unless otherwise indicated.

[a] De Yong and Lu (1998).

[b] McLain (1980).

around the particles is shed and "fresh" fuel atoms are exposed for oxidation. Since the system at this point is well above the Tammann temperature of magnesium, diffusion of oxygen (from the oxidizer) can occur into the metal lattice and ignition results. The potassium chlorate systems, as discussed above, tend to show ignition temperatures often well below the melting point of the fuel, even with magnesium as the fuel, owing to the low Tammann temperature and exothermic heat of decomposition.

It has also been shown that ignition temperature can be influenced by particle sizes in controlled experiments (Zhu, et al. 2014). Different particle sizes of spherical magnesium powder were mixed with different particle sizes of potassium nitrate, strontium nitrate, and potassium perchlorate. In one case, the average ignition temperature of a magnesium/100-mesh potassium nitrate mixture was found to be 626.3°C, while the same mixture with a 400-mesh potassium nitrate (much smaller) was found to be 605.4°C, over 20° lower. Notably, this effect was not seen with strontium nitrate or potassium perchlorate variation in size. However, a similar result was seen when the magnesium size was varied with all three oxidizers: as the size of the magnesium was reduced from 100 mesh to 400 mesh sized, the so-called "spontaneous reaction temperature," or temperature where exothermic reaction is taking place before true ignition, was reduced by 12°C for potassium nitrate, by 17°C for strontium nitrate, and by 23°C for potassium perchlorate. One can conclude that reduced particle sizes leads to greater surface interaction, greater particle packing, and/or greater heat retention that leads to a lowered observed ignition temperature.

METHODS FOR DETERMINING IGNITION TEMPERATURES

A review of ignition temperatures found in the pyrotechnic literature may well reveal a substantial variation in reported values for the same composition. This is often due to differences in the experimental conditions employed to measure the temperature corresponding to ignition. The weight ratio of components, degree of mixing, loading pressure (if any), heating rate, and quantity of sample can all influence the observed ignition temperature, not to mention particle sizes, moisture content, and any human-factor differences. As such, *the ignition temperature of a particular energetic mixture is not a fundamental constant*; ignition temperatures reported by different groups using different experimental methods may vary by as much as ±25°C, or more, for the same composition. Which number is correct? They all probably are, and each is a function of the specific experimental procedure that was employed. As differential scanning calorimetry (DSC) has evolved into the primary, generally agreed-upon method used to determine ignition temperatures for energetic materials, however, so the range of values reported for pyrotechnic mixtures has narrowed.

The legacy method for measuring ignition temperatures, used extensively by Henkin and McGill in their classic studies of the ignition of explosives (Henkin and McGill 1952), consisted of placing small quantities (3 or 25 mg, depending on whether the material was expected to denotate or deflagrate) of composition in a constant-temperature bath and measuring the time required for ignition to occur. The bath temperature was then raised a few degrees, and the experiment was repeated. Ignition temperature was defined, using this technique, as the bath temperature at which ignition occurs in 5 s. Data obtained in this kind of study can be plotted to yield interesting information, as shown in Figure 6.7. Not only will the researcher understand where instantaneous ignition *will* occur but also where delayed ignition *can also* occur, for storage safety and transportation purposes.

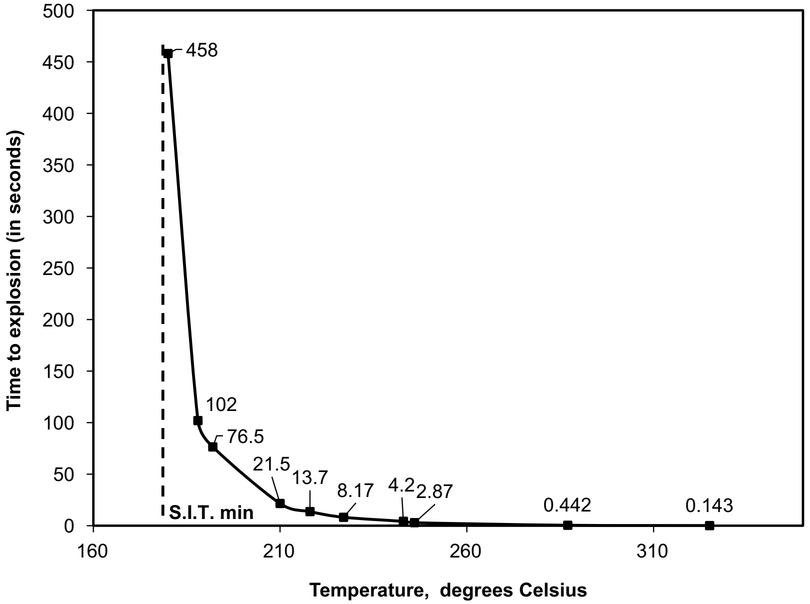


FIGURE 6.7 Time to explosion versus temperature for nitrocellulose (Henkin and McGill 1952). As the temperature of the heating bath is raised, the time to explosion decreases exponentially, approaching an instantaneous value. The extrapolated temperature value corresponding to infinite time to explosion is called the spontaneous ignition temperature, minimum (S.I.T. min).

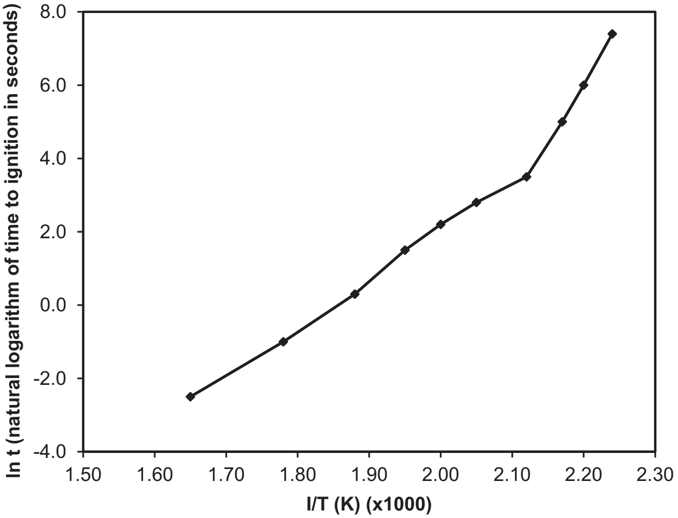


FIGURE 6.8 "Henkin–McGill Plot" for nitrocellulose (Henkin and McGill 1952). The natural logarithm of the time to ignition is plotted versus the reciprocal of the absolute temperature (K). An essentially straight line is produced, and activation energies can be calculated from the slope of the line. The break in the plot near 2.1 may result from a change in the reaction mechanism at that temperature.

Data from time versus temperature studies can also be plotted as natural-log time vs. 1/temperature, yielding generally straight lines as predicted by the Arrhenius Equation (see Chapter 2). Figure 6.8 illustrates this concept, using the same data plotted in Figure 6.7. Activation energies can be obtained from the slope of such plots: in this case, reported to be 26.5 kg-cal (Henkin and McGill 1952). Deviations from linear behavior and abrupt changes in slope are sometimes observed in Arrhenius plots due to changes in reaction mechanism or other complex factors.

"Henkin–McGill" plots can be quite useful in the study of ignition, providing us with important data on temperatures at which spontaneous ignition might occur. These data can be especially useful in establishing maximum storage temperatures for high-energy compositions; the temperature should be one corresponding to *infinite* time to ignition, and well below the "spontaneous ignition temperature," minimum—S.I.T. (min)—shown in Figure 6.7. At any temperature above this point, ignition during storage is likely to occur. Ignition might *also* occur at temperatures *below* a reported S.I.T. min point, however as the mass of the stored material increases, there is an increased risk for excessive self-heating within the material since the heat cannot dissipate as easily and may compound into viable ignition conditions. Therefore, S.I.T. studies on small samples should never serve as the sole basis of a thermal stability hazard analysis, certainly for bulk material.

Ignition temperatures, determined by DSC, usually correspond reasonably well to those obtained by a Henkin–McGill study. DSC values tend to be more reproducible from laboratory to laboratory and from sample to sample. Differences in heating rate, sample size, homogeneity, etc. can cause *some* variation in values obtained with thermal analysis technique. For *any* direct comparison of ignition temperatures, it is best to run all of the mixtures of interest under identical experimental conditions, thereby minimizing the number of variables. As an interesting case study, using the Henkin–McGill study above, the "lowest explosion temperature," or S.I.T. min, was reported to be 175°C, with an ignition temperature under 1 s of heating at 287°C. A recent study by H. Ma and associates reports, by DSC, that nitrocellulose shows the onset of heat flow at ~190°C and peak heat flow (decomposition) around 210°C with a heating rate of 10°C/min (Ma and al. 2017). At that same temperature, 210°C, Henkin and McGill report a time to explosion of 21.5 s. So, both studies show a similar lowest reported temperature resulting in ignition or heat flow.

One must also keep in mind that these experiments are measuring the *temperature sensitivity* of a particular composition, in which the entire sample is heated to the experimental temperature. Ignition sensitivity can, and must, *also* be discussed in terms of the relative ease of ignition of a small portion of a pyrotechnic material due to other types of potential stimuli, including static spark, impact, friction, and flame. Sensitivity to ignition is discussed further in Chapter 7.

SUMMARY OF IGNITION

For ignition to occur with an energetic mixture, a temperature must be reached (in at least a portion of the sample) where the oxidizer has been raised to a temperature where the evolution of oxygen is occurring at a significant rate and a fuel must be in a state where it can readily react with the released oxygen. In practice, the "activation" temperature for an oxidizer is usually observed to be a temperature approaching the melting point of the oxidizer (and therefore well past the Tammann temperature). For metallic and elemental fuels, the "activation" temperature is usually found to be near the melting point of the fuel—this is the temperature where any oxide coating will melt away, exposing fresh, reactive fuel atoms, as well as a temperature where diffusion of a mobile species is possible within the solid material. For organic fuels, the "activation" temperature should correspond to the decomposition temperature of the organic molecule, with the formation of readily oxidizable "free radicals" that will react with oxygen from the oxidizer to produce heat and propagate the reaction.

In summary, major ignition factors include (but are not limited to) the following:

1. Selection of oxidizer, fuel, and other components
2. Particle sizes of oxidizer and fuel
3. Grain size of the homogeneous composition (if present as granular material)
4. Type and amount of energy input
5. The presence of any sensitizers, intentional or unintentional

PROPAGATION OF BURNING

INTRODUCTION AND MEASURING PROPAGATION

The ignition process, ideally, initiates a self-propagating, high-temperature chemical reaction at the surface of the energetic mixture. The rate at which the reaction then

proceeds through the remainder of the composition will depend on the nature of the oxidizer and fuel, as well as on a variety of other factors.
"Rate" can be expressed in two ways:

1a. mass reacting per unit time (g/s); or
2a. length burned per unit time (cm/s).

Alternatively, rate can be expressed as the *reciprocal* of these units:

1b. the time required to burn a given mass of material (s/g); or
2b. the time required to burn a given length of material (s/cm).

The loading pressure used, and the resulting density of the composition, will determine the relationship between rates involving length and mass.

EFFECTS FROM COMPONENT SELECTION

Reaction velocity is primarily determined by the selection of the oxidizer and fuel (along with a *large* number of other factors, as we shall see). The rate-determining step in many high-energy reactions appears to be an endothermic process, with decomposition of the oxidizer frequently the key step. The higher the decomposition temperature of the oxidizer, and/or the more endothermic its decomposition, the slower the burning rate will be (with all other factors held constant).

Shimizu reports the following reactivity sequence for the most common of the fireworks oxidizers (Shimizu 1981):

$$KClO_3 > NH_4ClO_4 > KClO_4 > KNO_3$$

Shimizu notes that potassium nitrate is of course not "slow" when used in black powder (in which the homogeneity is maximized by extended energetic mixing) as well as in metal-containing compositions in which a "hot" fuel is present. Sodium nitrate ($NaNO_3$) is quite similar to potassium nitrate in reactivity (but is considerably more hygroscopic, a major factor in both ignition as well as burn rate if the mixture has excessive water present). Shidlovskiy has gathered data on burning rates for some of the common oxidizers (Shidlovskiy 1964). Table 6.5 contains data for oxidizers with a variety of fuels. Again, note the high reactivity of potassium chlorate.

The fuel also plays an important role in determining the rate of combustion. Metal fuels, with their highly exothermic heats of combustion and excellent thermal conductivity values, tend to increase the rate of burning. The presence of low-melting, volatile fuels (sulfur, for example) tends to *retard* the burning rate although they *enhance* ignitibility. Heat is used up in melting and vaporizing these materials rather than going into raising the temperature of the adjacent layers of unreacted mixture and thereby accelerating the reaction rate. To put another way, sulfur improves ignition but degrades propagation.

The higher the activation temperature of a fuel (generally its melting point or decomposition temperature), the slower is the burning rate of compositions containing the material, again with all other factors equal. Shidlovskiy notes that aluminum compositions are slower burning than corresponding magnesium mixtures due in part to this phenomenon (Shidlovskiy 1964).

TABLE 6.5
Burning Rates of Stoichiometric Binary Mixtures[a]

	Linear Burning Rate (mm/s)			
	Oxidizer			
Fuel	**$KClO_3$**	**KNO_3**	**$NaNO_3$**	**$Ba(NO_3)_2$**
Sulfur	2	X	X	–
Charcoal	6	2	1	0.3
Sugar	2.5	1	0.5	0.1
Shellac	1	1	1	0.8

Note: Compositions were pressed in cardboard tubes of 16 mm diameter. X indicates that the mixture did not burn.

[a] Shidlovskiy (1964).

EFFECTS FROM MASS RATIO AND STOICHIOMETRY

Stoichiometric mixtures should be expected—initially and logically—to be the fastest burners and this is observed when the oxidizer and fuel have similar thermal conductivities (such as an oxidizer/organic fuel mixture). Sometimes it is difficult to predict exactly what the actual preferred reaction(s) will be at the high-reaction temperatures encountered with these systems, so a trial-and-error approach is often advisable. A series of mixtures should be prepared by varying the fuel–oxidizer ratio above and below the stoichiometric point while keeping everything else constant. The formulation yielding the maximum burning rate is then experimentally determined.

When a *metal* fuel is present, expect the system to show increasing burn rates as the metal percentage is increased beyond the stoichiometric point, due to the increased thermal conductivity of the system as the metal percentage increases. The extra metal helps to capture more of the heat produced by the reaction and effectively transfers this heat into the next layer of composition (see below), raising the temperature closer to the ignition point. Table 6.6 shows how stoichiometry affects the burn rate of a binary strontium nitrate–magnesium red flare composition. The fuel-rich composition has the fastest burn rate and the highest candlepower, while the oxidizer-rich composition, as expected, burns

TABLE 6.6
Stoichiometry Effect on Burn Rate[a]

	Stoichiometric	Oxidizer-Rich	Fuel-Rich
% Magnesium (fuel)	36.3	28.8	42.8
% Strontium Nitrate	63.7	71.2	57.2
Burn rate (in/sec)	0.12	0.059	0.16
Candlepower (max.)	1,400	180	5,100

Note: Composition was pressed at 70 K psi.

[a] Puchalski (1974).

TABLE 6.7
Burn Rate of an Illuminant Composition vs. Binder Percentage[a]

% Magnesium	% Sodium Nitrate	% Binder	Burn Rate (in/sec)	Candlepower
55	39	6	0.139	291,800
55	37	8	0.106	240,700
55	35	10	0.094	195,000
55	33	12	0.088	180,600

Notes:

Magnesium was Type 1, ellipsoidal, –30/+50 mesh.

Sodium nitrate was 55 micron by sieve, 20 micron by Fisher sub-sieve sizer.

Binder was epoxy resin/polysulfide mix.

Flares were pressed at 14,000 psi in 2 increments.

[a] Diercks, et al. (1982).

the slowest and the dimmest. Table 6.7 shows the effect of varying the metal fuel–binder (organic fuel) ratio while keeping the relative oxidizer percentage constant. Reducing the metal percentage (as compared to the binder) in the mixture and increasing the binder percentage slows up the burn rate and reduces the candlepower of the sodium nitrate–magnesium illuminant mixture.

Effect from Other Factors: Heat Transfer, Loading Density, and Moisture

The transfer of heat from the burning zone to the adjacent layers of unreacted composition is also critical to the propagation/overall-combustion process. Metal fuels aid greatly here, due to their high thermal conductivity. For binary mixtures of oxidizer and fuel, combustion rate increases as the metal percentage increases, well past the stoichiometric point (as noted above). For magnesium mixtures, this effect is observed up to 60%–70% magnesium by weight and similar effects have been observed with other metal fuels, including tungsten, molybdenum, and zirconium. This behavior results from the increasing thermal conductivity of the composition with increasing metal percentage. With magnesium, a metal with a low boiling point around 1,100°C, excess magnesium that is vaporized by the heat evolved from the pyrotechnic reaction between oxidizer and fuel can react with oxygen from the atmosphere (De Yong and Lu 1998) and thereby can provide additional enhancement of the reaction rate as well as light output.

Variation in loading density, achieved by varying the pressure used to consolidate the composition in a tube, can also affect the burning rate. A "typical" high-energy reaction evolves a substantial quantity of gaseous products and a significant portion of the actual combustion reaction occurs in the vapor phase. For these reactions, the combustion rate (measured in grams consumed/second) will increase as the loading density *decreases*. A lightly consolidated, porous powder should burn the fastest, perhaps reaching an explosive velocity, while a highly consolidated mixture, loaded under considerable pressure, will burn slower. The combustion front in such mixtures is carried along by hot gaseous products. The more *porous* the composition is, the faster the reaction should be. The "ideal" fast composition is one that has been granulated to achieve a high degree of dense homogeneity *within* each particle but yet consists of small grains of powder with high surface area gathered *loosely* together. Burning will accelerate rapidly through a loose collection of such particles.

The exception to this "loading pressure rule" is the category of "gasless" compositions, such as the barium chromate/boron or iron oxide/silicon systems. Here, burning is believed to propagate through the mixture without the significant involvement of the vapor phase, and an increase in loading pressure should lead to an increase in burning rate, due to more efficient heat transfer via tightly compacted solid and liquid particles. Thermal conductivity is quite important in the burning rates of these compositions. Table 4.7 illustrates the effect of loading pressure for the "gasless" barium chromate/boron system: the higher the loading pressure, the faster the burn.

The presence of moisture can greatly retard the burning rate by absorbing substantial quantities of heat through vaporization. This book's repeated axiom "Keep your powder dry" has a scientific basis: the heat of vaporization of water—540 cal/g at 100°C—is one of the largest values found for liquid materials. It takes a large amount of heat to remove all of the water, and a composition cannot get hotter than 100°C until all water (acting as a heat sink) has been removed. To put it another way, considerable heat is required to remove each gram of water that would otherwise go to heating and igniting the intended energetic materials. Benzene, C_6H_6, as a contrasting example of a liquid with substantially weaker intermolecular attractive forces, has a heat of vaporization of only 94 cal/g at its boiling point, 80°C.

EFFECT OF EXTERNAL PRESSURE AND CONFINEMENT

The gas pressure (if any) generated by the combustion products, combined with the prevailing atmospheric pressure, will also affect the burning rate. The general rule here predicts that an increase in burning rate will occur as the external pressure increases. The ambient external pressure will act as confinement to gas products and heat attempting to escape from the reaction zone. This causes more of the heat to be retained by the burning composition, thereby accelerating the burn rate of the composition. This factor can be especially important when oxygen is a significant component of the gaseous phase, and the oxygen remains in the reaction zone for a longer time, thereby increasing the probability it will react with fuel. The magnitude of the external pressure effect indicates the extent to which the vapor phase is involved in the combustion reaction.

The effect of external pressure on the burning rate of black powder and numerous other propellants has been quantitatively studied. The general equation for the burn rate of a propellant is:

$$\text{Burn rate}(\text{m/s}) = ap^{\alpha} \tag{6.2}$$

where the term "*a*" represents the chemistry and engineering of the system, *P* represents the pressure in the burn chamber, and α (alpha) is the exponential coefficient that is a constant for the given propellant material. The "gassier" the propellant is in terms of reaction products, the higher the alpha value should be. Propellants are discussed further and some typical a (pre-exponential) and alpha (exponential) values for several propellants are given in Chapter 9. As shown in this later chapter, a nitroglycerine/nitrocellulose "smokeless powder" has a slower burn rate than black powder at 1 atmosphere. However, at high pressures, such as those typically found in the firing chambers of guns, the smokeless powders will significantly surpass black powder in burn rate.

Shidlovskiy reports the experimental empirical equation for the combustion of black powder to be

$$\text{Burn rate} = 1.21P^{0.24}\,(\text{cm/s}) \tag{6.3}$$

where P = pressure, in atmospheres. Predicted burning rates for black powder, calculated using this equation, are given in Table 6.8.

This increase in burn rate with confining pressure is a phenomenon that is well-known and widely used in designing propellant devices. A restrictor, or "choke," is often used in such devices to build up a higher internal pressure, and thereby speed up the propellant burn rate, and create more thrust.

For "gasless" heat and delay compositions, little external pressure effect is expected (as opposed to the strong effect from *loading* pressure). This result, plus the increase in burning rate observed with an increase in loading pressure, can be considered good evidence for the absence of any significant gas-phase involvement in a particular combustion mechanism. For the ferric oxide/aluminum (Fe_2O_3/Al), manganese dioxide/aluminum (MnO_2/Al), and chromic oxide/magnesium (Cr_2O_3/Mg) systems, some slight gas phase involvement is indicated by the three to four fold rate increase observed as the external pressure is raised from 1 to 150 atm. The chromic oxide/aluminum system, however, reportedly burns at exactly the same rate—2.4 mm/s—at 1 and 100 atm; suggesting that it is a true "gasless" system (De Yong and Lu 1998).

Data for the burning rate of a potassium permanganate/chromium delay system as a function of increasing external pressure (a nitrogen atmosphere was used) are given in Table 6.9

TABLE 6.8
Predicted Burning Rates for Black Powder at Various External Pressures[a]

External Pressure (atm)	External Pressure (psi)	Linear Burning Rate (cm/s)
1	14.7	1.21
2	29.4	1.43
5	73.5	1.78
10	147	2.10
15	221	2.32
20	294	2.48
30	441	2.71

Note: The Shidlovskiy equation is valid for the pressure range 2–30 atm.
[a] Shidlovskiy (1964).

TABLE 6.9
Burning Rate of a Delay Mixture as a Function of External Pressure[a]

Composition	Potassium Permanganate, $KMnO_4$	64%
	Antimony	36%

External Pressure (psi)	Burning Rate (cm/s)
14.7	0.202
30	0.242
50	0.267
80	0.296
100	0.310
150	0.343
200	0.372
300	0.430
500	0.501
800	0.529
1,100	0.537
1,400	0.543

Note: Compositions were loaded into 105 mm brass tubes at a loading pressure of 20,000 psi.

[a] Glasby (n.d.).

Another matter to consider is whether or not pyrotechnic compositions will burn, and at what rate, at very low pressure. For reactions that use oxygen from the air as an important part of their functioning, a substantial drop in performance is expected at low pressure. Mixtures high in fuel (such as the magnesium-rich illuminating compositions) will not burn well at low pressures since they require atmospheric oxygen to perform as intended. Stoichiometric mixtures—in which all oxygen needed to burn is provided by the oxidizer—should be the least affected by pressure variations. Data for burn rate of a delay mixture as the ambient pressure is reduced below one atmosphere are given in Table 6.10, and the burn rate is observed to slow up, as predicted, at lower pressures.

An interesting study by Schneitter on the ignition and performance of flash powder and black powder at low ambient pressures showed that attempts to ignite either potassium perchlorate–aluminum flash powder composition or commercial grade FFFg black powder using electric matches in a vacuum were unsuccessful, whereas the material readily ignited at normal atmospheric pressure (Schneitter and Schneitter 1998). The compositions *could* be ignited under the same vacuum conditions using an incandescent Nichrome wire filament (a nickel-chromium alloy that can heat to over 1,000°C), but ignition delays of up to 3.5 s were observed. Oxygen gas was shown not to be the critical factor, as the compositions ignited normally by

TABLE 6.10
The Effect of Low Ambient Pressure on the Burn Rate of a Delay Composition[a]

External Pressure, P (atm)	Burn Rate (mm/s)
1.0	16.9
0.74	16.0
0.50	15.9
0.26	15.5
0.11	14.9

Note: The delay composition is 30% boron and 70% bismuth trioxide. This delay has been used in the UK for many years. The delay system provided burn rates from 5 to 35 mm/s, as the amount of boron was varied. The maximum rate occurred with 15% boron.

[a] Davies, et al. (1985).

means of an electric match in one atmosphere of either helium or nitrogen gas, both inert for pyrotechnic purposes. This suggests that atmospheric pressure of any gas was important for ignition, not necessarily being ambient oxygen.

EFFECT OF EXTERNAL TEMPERATURE

As discussed in Chapter 2, rates of chemical reactions increase as ambient temperature increases. It can be anticipated that ease of ignition and burning rate will depend on the initial temperature of an energetic composition. Ignition of a cold composition will require more energy input for the initial layer or grain of composition to reach its ignition temperature. In a thermodynamic sense, more thermal input is needed to raise the composition to the activation energy at lower temperatures than at higher temperatures. The effect should be most pronounced for compositions of low exothermicity and high-ignition temperature.

Pyrotechnic and propellant devices that have been conditioned at a low temperature are also expected to burn slower than identical devices that have been conditioned at warmer temperatures. This is due primarily to the fact that the temperature rise that is required, via heat transfer from the reaction zone, for the succeeding layer of material to go from its initial temperature to the ignition temperature is a larger value for a cold device than a warm one.

Hence, the temperature at which devices are stored just preceding their use can be a factor in the performance of the items, if no temperature equilibration to a standard value is provided prior to use. In research and development work, it is important to eliminate variation in the temperature of end items when burn rates or burn times are measured. The effect of ambient temperature on the burn rate of a delay composition is shown in Table 6.11. In this case, the effect, while present, is relatively minor in this system, with a variation of approximately 10% over the wide temperature range that was studied, from very cold to very warm.

TABLE 6.11
Effect of Ambient Temperature on Burn Rate of a Delay Composition[a]

Temperature (°C)	Burning Time (s)
–40	3.43±0.13
Ambient/~25	3.30±0.07
165	3.15±0.14

Composition: Potassium perchlorate (33%), red iron oxide (18%), and tungsten (49%).

Loading pressure: 36,000 psi, column length approx. 0.64 in.

[a] Taylor, et al. (1991).

For black powder, a 15% slower rate is reported at 0°C versus 100°C, at external pressure of one atmosphere (De Yong and Lu 1998). For a boron/"red lead" oxide (B/Pb_3O_4) delay composition, the burning rate increased anywhere from 7% to over 16% when the ambient temperature increased from –50°C to 70°C, depending on the amount of boron by weight in the system. Interestingly, in this work, the burn rate increased in a *linear* fashion as the ambient temperature increased, while an increase in the amount of boron (from 1% to 16% by weight) showed a *logarithmic* increase in burn rate (Li, et al. 2010). This suggests that ambient temperature has a fairly straightforward effect on burn rate, while further reinforcing the idea that changes in material composition are much more complex and have several nuanced effects on burn rate.

Some high explosives show an even greater temperature sensitivity. The detonation velocity of nitroglycerine, for example, is 2.9 times faster at 100°C than it is at 0°C (De Yong and Lu 1998).

In summary, colder energetic devices will require more ignition stimulus, and burn slower, than warmer devices, with all other factors being equal.

BURNING SURFACE AREA

The burning rate—expressed either in g/s or mm/s—should increase as the burning surface area increases. Small grains will burn faster than large grains due to their greater surface area per gram. Compositions loaded into a narrow tube should burn more slowly than the same material in a wide tube. The heat loss to the walls of the container is less significant for a wide-bore tube, relative to the heat retained by the composition. For each composition, and each loading pressure, there will be a minimum diameter capable of producing stable burning as experimentally determined. This minimum diameter will decrease as the exothermicity of the composition increases; that is, when more heat is produced, more heat is available in the composition to propagate the burn even though some is lost to the container walls.

A thick-walled metal tube is particularly effective at *removing* heat from a burning composition and propagation of burning down a narrow column can be difficult for all but the hottest of mixtures, if metal (particularly a thick metal tube) is used for the container material. Recall that metal is a good conductor of heat and also has a good "heat capacity" to hold on to the heat. On the other hand, the use of a metal wire for the *center* of the popular wire "sparkler" retains the heat evolved by the barium nitrate–aluminum reaction and *aids* in propagating the burning down the length of the thin pyrotechnic coating.

A mixture that burns well in a narrow tube may possibly reach an explosive velocity in a thicker column, so careful experiments should be done any time a diameter change is made. For narrow tubes, one must also consider the generation of solid reaction products (ash) and their effect on burning. The ash produced, unless successfully ejected from the tube by hot gas or falling away, could create restriction in the tube, thereby preventing the escape of gaseous products. From the buildup of hot gases, an explosion may result if this occurs, especially for fast compositions.

DEFLAGRATION-TO-DETONATION TRANSITIONS (DDT)

Recalling the earlier discussion about *deflagration*, which can be thought of as an extremely fast, explosive combustion that appears to be instantaneous to human observers. That process is different compared to *detonation*, which can be thought of as a "shattering" of molecules from a pressure zone/shockwave created by a high-energy output in a short period of time. When a material detonates, the incident or initial shock creates a zone of high pressure (referred to as a detonation wave) which, as it enters into the zone of unreacted material, compresses and heats these unreacted materials to the point of essentially "pulling apart" chemical bonds, leaving molecular and atomic fragments in the wake of the shock. These fragments will rapidly recombine, releasing energy, propagating the detonation wave. Detonations progress at over 1,000 m/s, sometimes up to 9,000 m/s in some military high explosives.

If the conditions are suitable, a deflagrating pyrotechnic material can increase in burn rate depending on various factors previously discussed: the nature of the chemicals and mixture, gas and heat production, and overall confinement. If the pressure reaches a critical point, the deflagration mechanism can "transition" into a full detonation shock (pressure) wave moving at 1,000 m/s or more. This is known as a deflagration-to-detonation-transition, or DDT. In this case, the reaction rate *rapidly* increases as the process undergoes DDT, quickly increasing the instantaneous energy output.

The nature of the chemicals, confinement, and total quantity of the bulk chemicals appear to be the driving factors in successful DDT, if the chemical components are able to successfully transition. Homogeneity of the mix also appears to be important to sustain the "shattering" mechanism and therefore sustains the shockwave, so smaller particle sizes are also crucial to attain DDT if desired. Higher heat/gas output and hotter flame temperatures will of course assist in a DDT. For example, a confined mixture of small particle sized aluminum–potassium perchlorate–sulfur composition is well-suited for a DDT. Primary explosives (such as lead azide) will immediately DDT upon ignition stimulus, being part of their nature and often the reason for their use.

Conversely, a *reverse* slow-down transition is also understood: a detonation-to-deflagration transition where the detonating material does continually not react fast enough to sustain a detonation wave, and the reaction front resumes combustion at subsonic speeds, or deflagration. For example, if bulk material that is intended to achieve complete detonation is not compressed sufficiently, the material can "loosen" and not suffer the same compression required to go through a detonation process.

SUMMARY OF BURN RATE

The burn rate of a pyrotechnic composition is determined by a large number of factors, and there is no one way to measure the burn rate. All of these factors must be controlled in the manufacturing process to produce items that give reproducible performance from day-to-day and month-to-month. Burn rate factors include, but are not limited, to the following:

- Selection of oxidizer, fuel, and other components
- Weight ratio of the components
- Particle sizes of the components
- Homogeneity of the blended composition
- Presence of moisture
- Consolidation pressure (of pressed materials)
- External pressure
- External temperature/temperature of the composition
- Atmospheric oxygen available (if necessary to the composition)

Therefore, to intentionally change a burn rate, without changing the hardware for a device or changing ambient conditions, the following are some of the options:

1. Change the starting chemicals (new oxidizer, new fuel, or both)
2. Change the oxidizer–fuel ratio
3. Change the particle size of one or more components
4. Add a catalyst or a retardant to the composition
5. Mix for a longer time to increase homogeneity of the composition

Some of these options may be feasible for a given burn rate problem. Most will require a reevaluation of the new material for sensitivity and will require a requalification of the material and the end item for most military applications if the tolerances in the specifications and technical drawings for a device are exceeded. Given all the factors that affect the burn rate of an energetic material, it is easy to see why there is not yet a gold-standard computer program one can use to predict a burn rate.

COMBUSTION FLAME TEMPERATURE

A pyrotechnic reaction generates a substantial quantity of heat, and the actual flame temperature reached by these mixtures is an area of study that has been attacked from both the experimental and theoretical directions (De Yong and Valenta 1989).

Flame temperatures can be measured directly, using special high-temperature optical methods. They can also be calculated (estimated) using heat of reaction data and thermochemical values for heats of fusion and vaporization, heat capacity, and transition temperatures. Calculated values tend to be higher than the actual experimental results, due to heat loss to the surroundings as well as the endothermic decomposition of some of the reaction products. Details regarding these calculations, with several examples, have been published (Military Pyrotechnic Series Part One, "Theory and Application" 1967).

Considerable heat will be used to melt and vaporize the reaction products. Vaporization of a reaction product is commonly the limiting factor in determining the maximum flame temperature. For example, consider a beaker of water at 25°C. As the water is heated, at one atmosphere pressure, the temperature of the liquid rises rather quickly to a value of 100°C. To heat the water over the temperature range of 25°C–100°C, a heat input of approximately 1 cal/g of water per degree rise in temperature is required. To raise 500 g of water from 25°C to 100°C will require:

$$\begin{aligned}\text{Heat required} &= (\text{grams of water})(\text{heat capacity})(\text{temp change})\\ &= (500\text{ g})(1\text{ cal/g}^\circ\text{C})(75^\circ\text{C})\\ &= 37{,}500\text{ cal}\end{aligned}$$

Once the water reaches 100°C, however, the temperature increase stops. A plateau is reached, and the water boils at 100°C. Liquid is converted to the vapor state, and 540 cal of heat (the heat of vaporization of water) are needed to convert 1 g of water from liquid to vapor. Note the substantial difference: 1 cal of heat to raise a gram of water 1° but 540 cal to vaporize the same gram of water once at boiling temperature. To vaporize 500 g of water, at 100°C,

$$(500\text{ g})(540\text{ cal/g}) = 270{,}000\,\text{cal}$$

We can calculate that 270 kcal of heat is required. Until this quantity of heat is put into the system, and all of the water is vaporized, no further temperature increase will occur in the system since all of the excess heat is going to vaporize water (and not further heat the flame). Similar phenomena involving the vaporization of pyrotechnic reaction products such as magnesium oxide (MgO) and aluminum oxide (Al_2O_3) tend to limit the peak temperature attained in pyrotechnic flames. The boiling points of some common combustion products are given in Table 6.12.

The experimentally measured flame temperatures of many oxidizer–magnesium compositions show values near 3,600°C (the boiling point of magnesium oxide); Oxidizer–aluminum compositions tend to produce flame temperatures near 3,000°C (the melting point of aluminum oxide). As a result, the intensity of the light emission from an oxidizer–magnesium flare will be considerably greater than that of a flare containing the same oxidizer mixed with aluminum. Remember, light emission from incandescing black bodies is proportional to temperature to the fourth power—that 600°C difference in flame temperature is *very* noticeable to the human eye. If you want a *really* bright, intense flame, the fuel material of choice would be zirconium—since the boiling point of ZrO_2 approaches 5,000°C. The brightness of this composition may be harmful to human eyes.

Mixtures using organic (carbon-containing) fuels usually attain lower flame temperatures than those compositions consisting of an oxidizer and a metallic fuel. This

TABLE 6.12
Melting and Boiling Points of Common Non-Gaseous Pyrotechnic Products[a]

Compound	Formula	Melting Point (°C)	Boiling Point (°C)
Aluminum oxide	Al_2O_3	2,072	2,980
Barium oxide	BaO	1,918	ca. 2,000
Boron oxide	B_2O_3	450	ca. 1,860
Magnesium oxide	MgO	2,852	3,600
Potassium chloride	KCl	770	1,500 (sublimes)
Potassium oxide	K_2O	350 (decomposes)	–
Silicon dioxide	SiO_2	1,610 (quartz)	2,230
Sodium chloride	$NaCl$	801	1,413
Sodium oxide	Na_2O	1,275 (sublimes)	–
Strontium oxide	SrO	2,430	ca. 3,000
Titanium dioxide	TiO_2	1,830–1,850 (rutile)	2,500–3,000
Zirconium dioxide	ZrO_2	ca. 2,700	ca. 5,000

[a] Weast (1994).

reduction in flame temperature can be attributed to the lower heat output of the organic fuels versus metals, as well as to some of the lower heat output going toward the decomposition and vaporization of the organic fuel and its by-products. The presence of even small quantities of an organic component (possibly added as a binder) in an oxidizer–metal fuel mixture can markedly lower the flame temperature, as the available oxygen is consumed by the carbonaceous material in competition with the metallic fuel (Tanner 1972). Table 6.13 illustrates this behavior, with data reported by Shimizu (Shimizu 1981).

This reduction of flame temperature can be minimized somewhat by using binders with high oxygen content. In such binders, the carbon atoms are already partially oxidized, and they will therefore consume less oxygen per gram (and per mole) than pure hydrocarbons in going to carbon dioxide during the combustion process. The balanced chemical equations for the combustion of hexane (C_6H_{14}) and glucose ($C_6H_{12}O_6$) illustrate this (both are six-carbon molecules):

$$C_6H_{14} + 9.5O_2 \rightarrow 6CO_2 + 7H_2O \tag{6.4}$$

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \tag{6.5}$$

(the second reaction uses less oxygen per mole of fuel as well as per gram of fuel)

Pyrotechnic flames typically fall in the 1,500°C–3,000°C range, with smoke and colored light compositions in the lower ranges and light–heat compositions at the higher range. Table 6.14 lists approximate values for some common classes of high-energy reactions (Shidlovskiy 1964).

Binary mixtures of oxidizer with metallic fuel yield the highest flame temperatures, and the choice of oxidizer does not appear to make a substantial difference in

TABLE 6.13
Effect of Organic Fuels on Flame Temperature of Magnesium/Oxidizer Mixtures[a]

Composition	Oxidizer	55% by weight
	Magnesium	45% by Weight
	Shellac	Either 0% or 10% Additional

	Approximate Flame Temperature (°C)	
	Oxidizer	
	$KClO_4$	$Ba(NO_3)_2$
Without shellac	3,570	3,510
With 10% shellac	2,550	2,550

Note: Temperature was measured 10 mm from the burning surface in the center of the flame.

[a] Shimizu (1981).

TABLE 6.14
Maximum Flame Temperature of Various Classes of Pyrotechnic Mixtures[a]

Type of Composition	Maximum Flame Temperature (°C)
Photoflash, illuminating	2,500–3,500
Solid rocket fuel	2,000–2,900
Colored flame mixtures	1,200–2,000
Smoke mixtures	400–1,200

[a] Shidlovskiy (1964).

the temperature attained (even if overall burn rates will vary). However, for compositions without metal fuels, this does not seem to be the case. Shimizu has collected data for a variety of compositions and has observed that potassium nitrate mixtures attain substantially lower flame temperatures than similar mixtures made with chlorate or perchlorate oxidizers with organic fuels. This result can be attributed to the substantially endothermic decomposition of KNO_3 relative to the other oxidizers combined with the lower heat output per gram of the non-metal fuels. Table 6.15 presents some of the Shimizu data (Shimizu 1981).

A final factor that can limit the temperature of pyrotechnic flames is unanticipated high-temperature chemistry. Certain reactions that do not occur to any measurable extent at room temperature become quite probable at higher temperatures. An example of this is the reaction between carbon (C) and magnesium oxide (MgO). Elemental carbon can be produced from organic molecules in the flame, if it is not fully oxidized to CO_2. If carbon and magnesium oxide are present, the following reaction is possible:

TABLE 6.15
Flame Temperature for Oxidizer/Shellac Mixtures[a]

Composition	Oxidizer	75%
	Shellac	15%
	Sodium Oxalate	10%

Oxidizer	**Approximate Flame Temperature (°C)**
Potassium chlorate, $KClO_3$	2,160
Potassium perchlorate, $KClO_4$	2,200
Ammonium perchlorate, NH_4ClO_4	2,200
Potassium nitrate, KNO_3	1,680

[a] Shimizu (1981).

$$C(\text{solid}) + MgO(\text{solid}) \rightarrow CO(\text{gas}) + Mg(\text{gas above } 1100°C) \tag{6.6}$$

This is a strongly *endothermic* process, but it becomes possible at high temperature due to a favorable entropy change: formation of the random vapor state from solid reactants. Recalling thermodynamics, increased entropy can be a major driver in whether one reaction takes place over another. Such reactions provide another reason for the lower flame temperatures achieved when organic binders are added to oxidizer/metal mixtures (McLain 1980). Again, the endothermic reaction will "soak up" all available energy that would otherwise go to increasing flame temperatures.

PROPAGATION INDEX

A simple method for assessing the ability of a particular composition to burn under adverse conditions is the "Propagation Index," originally proposed by McLain (McLain 1980) and later modified by Rose (Rose 1971). The original McLain expression was as follows:

$$PI = \Delta H_{\text{reaction}} / T_{\text{ignition}} \tag{6.7}$$

where PI—the Propagation Index—is a measure of a mixture's tendency to sustain burning upon initial ignition by external stimulus. The equation contains the two main factors that determine burning ability: the amount of heat released by the chemical reaction and the ignition temperature of the mixture in Kelvin. If a substantial quantity of heat is released and the ignition temperature is low, then re-ignition from layer to layer should occur readily and propagation is likely. Conversely, mixtures with low-heat output and high-ignition temperature should propagate poorly, if at all. Propagation index values for a variety of compositions are given in Table 6.16. The temperatures used in these calculations were the Celsius rather than Kelvin values.

Rose recommended modifying the original McLain expression by the addition of terms for the pressed density of the composition and for the burning rate of the mixture. He reasoned, especially for delay compositions compressed in a tube, that

TABLE 6.16
Propagation Index Values for Pyrotechnic Mixtures (Rose 1971)

	Composition	% by Weight	Heat of Reaction (cal/g)	Ignition Temperature (°C)	Propagation Index (cal/g °C)
I.	Boron igniter		1,600	565	2.8
	Boron	23.7			
	Potassium Nitrate	70.7			
	Laminac resin	5.6			
II.	Black powder		660	330	2.0
	Potassium nitrate	75			
	Charcoal	15			
	Sulfur	10			
III.	Titanium igniter		740	520	1.4
	Titanium	26			
	Barium chromate	64			
	Potassium perchlorate	10			
IV.	Manganese delay		254	421	0.60
	Manganese	41			
	Lead chromate	49			
	Barium chromate	10			

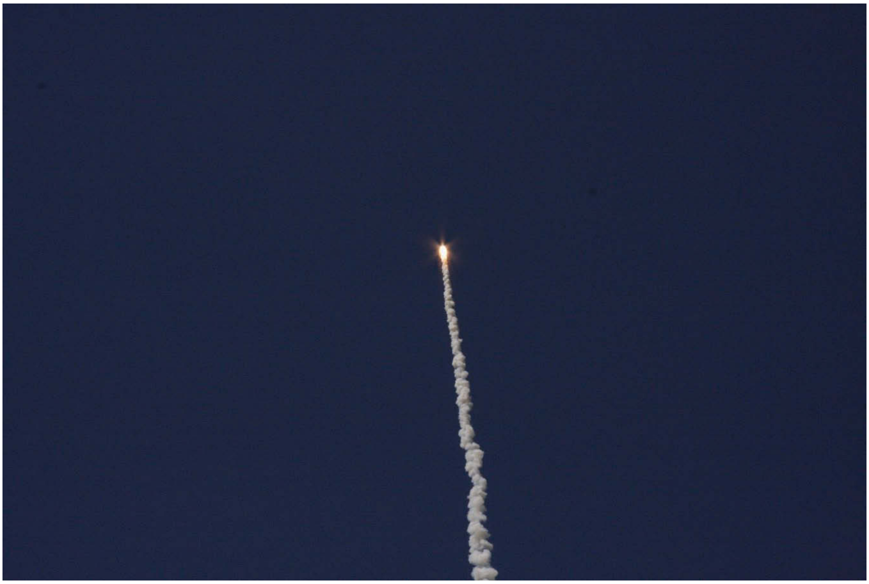
[a] Shidlovskiy (1964).

ability to propagate should increase with increasing density, due to better heat transfer between grains of composition. Burning rate should also be a factor, he argued, because faster-burning mixtures should lose less heat to the surroundings than slower compositions (Rose 1971).

IGNITION AND PROPAGATION: A FINAL NOTE

Ignition and subsequent propagation of energetic compositions require a sufficient energy stimulus to initiate the burn and sufficient evolved energy to initiate the ignition of the next layer. Numerous factors will affect the amount of energy needed for a particular composition and how fast the propagation—the burn rate—will continue. The materials involved, their weight ratios, the amount of mixing, the particle sizes, the presence of moisture, the loading pressure, and the ambient conditions (temperature, pressure, gaseous oxygen) will all affect the overall ignitability and performance of a given pyrotechnic mixture.

7 Sensitivity



COMET IN AIR: A large pellet of light-producing pyrotechnic composition, fired into the air, is referred to as a "comet". These can be used for entertainment as well as emergency signaling purposes. Duration of the burn and size of the effect are determined by both the chemistry that is used as well as the actual mass of the pellet. The compositions must possess sensitivity characteristic such that they are safe to press into compacted pellets, yet light reliably when they are fired into the air.

> An energetic material is of little value if you cannot safely mix it, load it into an end item, store it, transport the manufactured device, *and* still have the device function properly when a reasonably mild (or requisitely strong) ignition stimulus is applied. This chapter gives a new meaning to the term "Sensitivity Training."

SENSITIVITY TESTING: AN INTRODUCTION

In investigating the "sensitivity" of an energetic material, the test engineer applies a controlled level of energy (in one of a variety of forms) to the material, and the system is observed for positive signs that a reaction has occurred: a flash of light, sparks, smoke, a characteristic odor, an audible report, or other pyrotechnic function. The "sensitivity" of an energetic mixture is not just a matter of significant research interest but it is also a matter of vital interest to the manufacturer of the mixture. Each energetic material must be sensitive to ignition, but yet only function when you want it to ignite in order to achieve reliable performance from a particular device. Some type of external energy input (not necessarily just heat or flame) is used to ignite the first component in the device, and as we saw in the preceding chapter, the remaining components in the device are in turn ignited by the output from the preceding component as the device sequentially functions.

One of the first things to know about "sensitivity" is the fact that it is a very complex subject. The only correct answer to a question like "Is this mixture sensitive?" is another question: "Sensitive to what?" A particular composition may be extremely sensitive to electrostatic spark but not have any heightened sensitivity to elevated temperature. Similarly, a friction-sensitive material may not be particularly sensitive to spark. Each mode of energy input interacts with the components of an energetic material in a different way. If the applied energy is effectively absorbed by the composition, a temperature rise may occur. If the rising temperature approaches the ignition temperature of the composition, ignition may result.

In some instances, the energy input is strongly absorbed by the mixture; in other systems, there is little transfer of energy to the composition. Hence, there is no alternative but to test each new composition for its "sensitivity" by running the whole scan of standard sensitivity tests: friction, impact, spark, and thermal, with shock sensitivity often measured as well.

IGNITION SENSITIVITY: A STATISTICAL EVENT

Another key point is that sensitivity has a *probability* factor associated with it—you can run sensitivity tests on a given energetic material and perform 10 tests at each energy level that is examined. At low levels of energy input, 0 of 10 trials produce a positive (ignition) result. Raise the energy input level and you may observe, perhaps, that the material ignites in six of ten trials. As you raise the energy level of the ignition stimulus even higher—be it friction, impact, or spark—the number of positive tests observed in 10 successive trials should continue to increase and reach 10 out of 10 positive results.

Ignition is a statistical event—the energy that is introduced into the sample must be effectively absorbed by the sample and a temperature rise must occur in at least part of the sample, bringing that portion to its ignition temperature. A sufficient amount of the sample must then in turn ignite in order for a "positive" result to be detected and recorded. There is not an "on/off" switch with respect to sensitivity—each sample as placed in the test fixture will have minor differences in content and orientation in the sample holder and the delivery of energy from the test apparatus will similarly vary slightly from test to test. The end result will be a probability curve. Figure 7.1 illustrates an "ideal" sensitivity curve one might develop after extensive research trials.

Low levels of energy input will result in close to zero ignitions of the sample. These values represent levels that will be associated with safety in manufacturing and subsequent handling of the energetic material. High levels of energy input should result in close to 100% ignition of test samples. These high levels represent the ability of the composition to produce reliable ignition of the material in an end item, if the proper ignition energy is provided by the engineer who designs the ignition mechanism for the item.

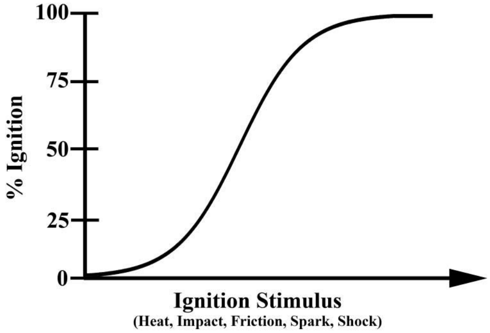


FIGURE 7.1 An "ideal" sensitivity curve. When very little energy stimulus is applied, ignition is non-existent. As more energy stimulus is applied, the probability of ignition increases to a point where ignition is (ideally) guaranteed with that amount of energy or greater. In a perfect world, the percent ignition up to a point would be 0%, with any ignition after that point 100%, however that is not the reality of pyrotechnics.

SENSITIVITY TESTING: SAFETY CONCERNS

During the manufacturing process, chemicals are initially mixed to produce a reasonably homogeneous blend of oxidizer, fuel, binder, and other components. These mixtures are then pressed into tubes, extruded as thick pastes, or otherwise processed in the manufacturing process. During these operations, it is possible that the chemical mixtures will experience impact, friction, spark, and heat. It is therefore extremely important that the manufacturer have knowledge of the sensitivity of all their energetic mixtures to each of these various types of energy input.

No energetic composition should be deemed truly "safe", however, even if it appears to be insensitive to a range of ignition stimuli. All pyrotechnic and propellant compositions are designed to function by burning or deflagration (very rapid burning), and a mixture that does *not* release its energy rapidly when exposed to a moderately energetic ignition source will be of extremely limited value. Manufacturers must have technical data on the sensitivity of their mixtures to ignition from various stimuli, and they must then analyze their manufacturing processes to determine all of the possible sources of energy that compositions might experience during mixing, loading, and assembly into finished devices. In a study by the U.S. Army, a systematic evaluation of the properties of a range of pyrotechnic compositions was carried out, using the identical test equipment, technician, and test procedures for all of the tested materials. This study provided a wealth of information on the factors that affect the sensitivity of pyrotechnic compositions (Aikman 1987).

The sensitivity of a high-energy mixture to an ignition stimulus is influenced by a number of factors. A mixture of an energetic fuel (e.g., aluminum) with an easily decomposed oxidizer (e.g., potassium chlorate, $KClO_3$) is expected be quite sensitive to a variety of ignition stimuli. A composition with a poor fuel and a stable oxidizer should be much less sensitive, if it can be ignited at all. Ignition temperature, as determined by thermal analysis or a Henkin–McGill time-to-ignition study, is but one measure of sensitivity, and there is not any simple correlation between ignition temperature and static spark, impact, or friction sensitivity (Henkin and McGill 1952). Some mixtures with reasonably high ignition temperatures (potassium perchlorate, $KClO_4$ mixed with fine-particle-size aluminum is a good example) can be quite spark-sensitive, because aluminum metal is an effective absorber of the energy in a spark, and the reaction is highly exothermic and becomes self-propagating once a small portion is ignited. Sensitivity and output are not necessarily related and are determined by different combinations of factors. A given mixture can have high sensitivity and low output, low sensitivity and high output, or any other combination of these two properties. McLain has proposed categorizing the relative hazards of pyrotechnic compositions based on the combination of these two properties (McLain 1980).

Those mixtures that have both high sensitivity and substantial output are the ones that must be treated with the greatest care. Potassium chlorate/sulfur/aluminum "flash and sound" mixture is an example of this type of dangerous composition, having both a low ignition temperature (<200°C) and significant spark sensitivity (depending heavily on the type of aluminum powder that is used). Potassium perchlorate/zirconium ignition composition (ZPP) is another composition that is *extremely* sensitive to spark, and it has seen increased use in recent years as an energetic ignition composition that very quickly produces very high flame temperatures when ignited (Durgapal 1988).

The ignition sensitivity of energetic compositions can vary considerably, depending on the *type* of energy interacting with the chemical mixture. It is necessary for a given energy input to be efficiently transferred to the composition for a temperature rise to occur and ignition to be achieved. Energy input may occur via impact or friction and thereby involve mainly energetic that is kinetic in nature. A spark is a combination of thermal, electrical, and shock input, while exposure of a composition to flame or heat involves the application of thermal energy.

To achieve ignition in systems that contain molecular fuels such as a sugar, oxygen-rich anions like chlorate or nitrate, or both, it is necessary for some chemical bonds in the mixture to absorb a sufficient quantity of the incident energy for bond breaking to occur. This energy transfer frequently involves raising the vibrational energy of various chemical bonds in the starting materials to the point where the restoring force is overcome, and the bond breaks, creating so-called "free radicals," or atoms/molecules with unpaired valence electrons. Reaction products then form from reaction between oxidizer and fuel, and a net release of energy occurs. If this released energy is sufficient in quantity, and is efficiently captured by adjacent layers or grains of blended chemical composition, the ignition process is repeated through the mixture, and propagation of the burning reaction is achieved with no additional input of external energy required. Sensitivity testing measures the minimum level of a specific type of energy input required to initiate the ignition process for a given energetic composition, under a specific set of test conditions.

VARIABILITY IN SENSITIVITY TESTING RESULTS

A number of specific types of test equipment have been developed over the past years for measuring sensitivity to elevated temperature, impact, friction, and electrical spark, and it is unfortunate that a universal test fixture for measuring each type of sensitivity has yet to be agreed upon by the international explosive and pyrotechnic community. Notably, though, the community has begun to focus on universal types of tests and apparatuses, such as the Bureau of Explosives impact test apparatus (the "BOE") used by both the U.S. Department of Defense and Department of Transportation, or the "BAM Friction" devices. However, test apparatuses vary from country to country and laboratory to laboratory, and there are even *multiple* types of impact and friction test equipment used within a given country or laboratory. Beneficially, the United Nations has produced a set of tests and criteria for studying both the sensitivity and output of energetic materials and devices containing energetic materials to create some uniformity (United Nations 2009).

It is therefore often difficult, if not impossible, to directly compare impact or friction sensitivity results obtained on different types of test equipment. It can also be difficult to directly compare results obtained from the same type of test apparatus used by a different test engineer in a different facility, with different ambient conditions. Each test apparatus has its own unique characteristics and each tester has his or her own slight difference in test procedures (recalling the "human factor" differences in preparing energetic mixtures). All of these variables can produce different test results. Relative *rankings* of sensitivities, however, generally bear some semblance of order, but quantitative comparisons between test laboratories are not advisable. Sensitivity testing by its very nature yields abstract results. The specific geometry of the test fixture, sample size, grain size, rate of energy delivery, and a host of other factors all contribute to the resulting sensitivity value. A change in any of these can alter the observed results, so caution is always needed.

So, how do we use sensitivity data? We use it by comparing the sensitivity of a new composition to other compositions with a history of manufacturing and handling safety. If the sensitivity results for a new material are comparable to a material with a history of accidents, special caution is called for. This approach only works when the sensitivity data are obtained using the same type of test apparatus, preferably using an identical device with the tests run by the same test operator. Even here, however, sensitivity of a particular composition to each type of energy input can vary from day-to-day and batch-to-batch should there be changes in particle size, moisture content, homogeneity, sample age, and chemical purities.

SPARK SENSITIVITY

Most spark sensitivity devices work on the general principle of using a variable voltage power supply to charge a capacitor, and then the resulting stored-up energy is discharged as an electrostatic spark through a needle-like tip (the cathode) into the sample under investigation, which rests on a positively charged anode (Skinner, et al. 1998). The energy of the spark can be calculated by the equation E (in Joules) = $\frac{1}{2}CV^2$, where C is the capacitance in farads and V is the voltage (in volts) from the power supply. This test is often called ESD for "electrostatic discharge." A mock-up drawing of an ESD is shown in Figure 7.2.

Experience has shown that the presence of certain fuels in pyrotechnic mixtures, particularly when present in fine particle size, tends to cause the resulting mixtures to have significant sensitivity to spark. Zirconium, boron, and phosphorus are particularly noted for their spark sensitivity. Fine magnesium or aluminum powder can

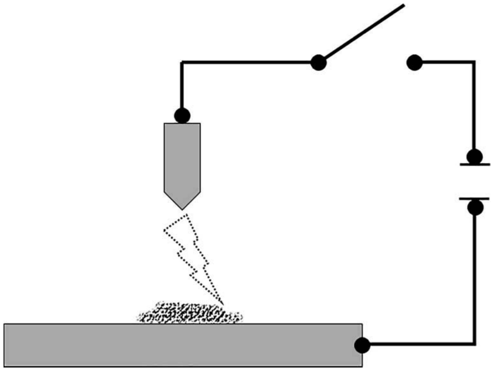


FIGURE 7.2 A mock-up drawing of an electrostatic discharge device (ESD). A sample of the pyrotechnic composition will be placed on the receiving plate (anode) and a needle-tip (cathode) will be brought nearer to the sample. Once an electrical spark discharge takes place, with energy depending on the capacitance and voltage set on the device, the electric spark will interact with the pyrotechnic material and yield a fire/no-fire result, observed by the analyst.

also enhance spark sensitivity, and fine-grains of blended oxidizer–fuel mixture will have a significantly greater sensitivity to spark than coarser grains. This is of importance to manufacturers, because there is always the possibility of generating fine pyrotechnic dust during processing.

Experience has also shown that the looseness of a mixture can also affect spark sensitivity, where a pressed pellet will have a reduced sensitivity to spark versus a loose pile of the same composition. However, this will vary from mixture-to-mixture, and no specific universal trend can be derived.

Spark sensitivities for metallic fuels will also vary greatly depending on the age of the fuel, as an oxide coating (e.g., Al_2O_3 on aluminum or MgO on magnesium) will "insulate" the metal from accepting the electric impulse, heating, and igniting. The sensitivity of a metal-containing composition may actually decrease as it ages and an oxide coating forms.

Spark sensitivity trends for specific pyrotechnic compositions tend to correlate fairly well from laboratory-to-laboratory when a minimum ignition energy, in joules (abbreviated "J"), is determined and starting chemicals similar in particle size and shape are used. In assessing spark-sensitivity hazard, a value of 0.10 J or less for spark ignition energy is often regarded as indicating a spark sensitivity concern requiring a full static protection program. This is because a moving human being can develop and hold a spark energy of approximately 0.015 J (15 mJ), so compositions and fuels that have spark ignition energies near this value are of particular concern in manufacturing and handling (Skinner, et al. 1998). The aforementioned "alarm" value of 0.10 J (100 mJ) adds a safety factor of >6 to the 15 mJ human spark energy value.

Vapors from organic solvents such as acetone and alcohol (often used to "activate" binders in the mixing process for energetic materials) can form mixtures with air that are both spark-sensitive and explosive, showing spark sensitivity values below 1 mJ in many cases. A layer of volatile, ignitable solvent may form at the surface of a drying energetic mixture, blend with atmospheric oxygen, and thereby create a serious spark hazard that persists until all the solvent has been removed. Many of these solvent-air mixtures are readily ignited by the energy in a human-generated spark. One safe solvent to use to eliminate spark sensitivity as a solvent concern is water, but water creates its own set of performance and aging problems with many pyrotechnic compositions (remember: Keep your powder dry!).

Spark sensitivity values for a series of pyrotechnic compositions are given in Table 7.1. It can be seen that these values tend to be considerably greater than

TABLE 7.1
Electrical Spark Sensitivities of Various Pyrotechnic Compositions[a]

Composition	Components	Weight Ratio	Minimum Electrical Spark Ignition(J)
Black Powder	Charcoal	15	3.125
	Potassium nitrate	75	
	Sulfur	10	
Military Ignition Mixture	Iron(III) oxide	25	0.0004
	Zirconium	65	
	Diatomaceous earth	10	
	VAAR binder	+1%	
Military First Fire Mixture	Lead oxide, Pb_3O_4	55	0.276
	Silicon	33	
	Titanium	12	
	Nitrocellulose binder	+1.8%	
Red Fireworks Stars	Charcoal	4	0.685
	Red gum	18	
	Potassium perchlorate	60	
	Strontium carbonate	18	
Military White Flare Mixture	Sodium nitrate	49	>50
	Magnesium (20/50 mesh)	40	
	Laminac polyester binder	11	
Chinese firecracker powder	Aluminum		0.056
	Sulfur		
	Potassium chlorate		
Flash powder (fine powder)	Dark "pyro" aluminum		
	FINE potassium perchlorate		0.032
	COARSE potassium perchlorate		0.980

Note: These values were obtained using a device patterned after the U.S. Bureau of Mines (BOM) electrical spark apparatus. The value reported is the minimum energy at which at least one sample in 10 ignited. These values are from Aikman et al. or were similarly determined by the late Fred McIntyre, formerly of Sverdrup Technology, Inc., Bay St. Louis, Mississippi, one of the authors of the Aikman et al. reference.

[a] Aikman (1987).

0.10 J, unless a fine metal powder (such as aluminum) is used. Keep in mind that sparks sensitivities can vary greatly for a given oxidizer–fuel mixture, with the particle size and surface oxidation state of the fuel often playing a very significant role. A manufacturer cannot rely on spark sensitivity results other than those obtained on compositions produced by their company and ideally on those obtained from batch-to-batch.

Knowing whether a given composition has the potential to be ignited by a static spark is important, keeping in mind that spark sensitivity for a given material can also vary from batch-to-batch, based on a number of other factors such as grain size, homogeneity, and humidity. A thorough Hazard Analysis—using the appropriate sensitivity data—must be done on each operation where there is exposed energetic material in order to determine the level of spark protection and worker protection that is required.

FRICTION SENSITIVITY

Friction sensitivity studies have shown a relationship to ignition temperature and heat of reaction, but the critical factor in friction sensitivity appears to be the presence in a composition of a significant amount of a "gritty" or hard, granular component. Such a material, when exposed to frictional action, will generate "hot spots" that can lead to ignition. Metal particles are a particular concern in the generation of frictional "hot spots." The addition of titanium to fine black powder has been shown to have a significant effect on the friction sensitivity as well as the impact sensitivity of the composition, as shown in Table 7.2 (Wharton, et al. 1993). Impact sensitivity increased as the proportion of titanium increased, while friction sensitivity was the greatest for compositions containing 20%–30% titanium metal by weight.

Several types of friction-sensitivity equipment are in current use in the energetic materials field, and they tend to differ significantly in the fundamental nature of their means of energy input into the test sample (United Nations 2009), such as the BAM

TABLE 7.2
Effect of Titanium Powder on Sensitivity of Black Powder[a]

% Ti	Impact (Figure of Insensitiveness)	Friction (Figure of Friction)
0	149	7.1
5	127	5.3
10	136	3.6
20	115	3.5
40	69	4.5
60	61	5.1

Notes: Titanium particle size was 355–500 micron. Black powder was fine "meal A" granulation. Lower values indicate greater sensitivity to ignition in these tests.

[a] Wharton, Rapley, and Harding (1993).

friction device, a rotary friction device, and even an “impact friction” device. The lack of a standard, quantitative method of evaluating friction sensitivity has limited the detailed evaluation of this type of energy input, but friction is always a concern when energetic compositions are pressed into tubes. The proper alignment of tools and equipment used in pressing operations is very important in minimizing the possibility of a friction-related incident.

The good news about friction sensitivity is that we know how to solve a friction problem—add a lubricant! The addition of a small amount of wax, oil, or other “smoothing” component to a friction-sensitive composition can dramatically reduce the friction sensitivity of the composition. The only question remaining is whether or not you have changed any *other* property of the composition by the addition of the lubricant. A small percentage of such an ingredient can alter the burn rate and ignition temperature, as well as other properties of the composition. A complete reevaluation of sensitivity and performance is always required when a new component is added to a composition, even in a low percentage. An example of the range of friction sensitivity that can be observed for pyrotechnic compositions, with and without the presence of lubricating components, is shown in Table 7.3, where the first two compositions contain significant metal powder and no lubricant, while the third composition contains significant lubricant and is quite insensitive to friction. Here, the lubricants are Teflon® and Viton® powder. Both chemicals are fluorine-containing organic molecules used as “non-stick” materials in cooking (Teflon®) and for industrial needs such as O-rings or molded parts (Viton®).

Mock-up drawings and pictures of ABL and BAM type friction testing devices are shown in Figures 7.3 and 7.4.

TABLE 7.3
Rotary Friction Sensitivities for Some Pyrotechnic Compositions[a]

Composition	Components	Weight Ratio	Ignition Energy(ft-lb^2/s)
IM 28 Incendiary	Barium nitrate	40	19
	Potassium perchlorate	10	
	Magnalium alloy	50	
SW522 Smoke	Potassium perchlorate	20	52
	Potassium nitrate	20	
	Aluminum	20	
	Zinc dust	40	
M22 Flash Mixture	Magnesium (−200/+325 mesh)	75	>55,041
“MTV”	Teflon	10	
	Viton	15	

[a] Aikman (1987).

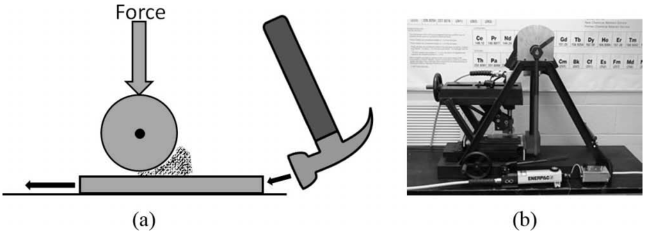


FIGURE 7.3 A mock-up drawing and a picture of an ABL™ Friction Test Apparatus. In (a), a pyrotechnic composition is placed on a sliding plate next to a static wheel, which has a certain force applied to it. A hammer will strike the plate, forcing the pyrotechnic material under the rolling wheel at a certain force, yielding a fire/no-fire result (which can also be tested by pressure-sensing device that will detect gas production from an ignition). (b) A picture of an actual ABL Friction Test Apparatus (picture courtesy of UTEC Corporation, LLC, http://www.utec-corp.com/).

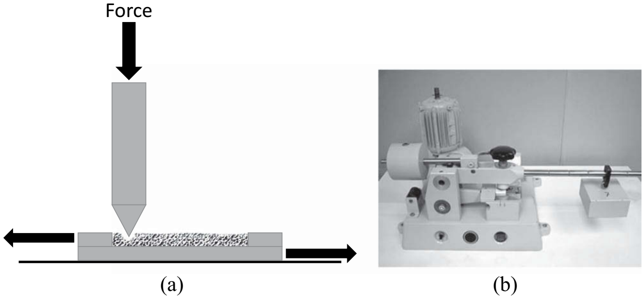


FIGURE 7.4 A mock-up drawing and a picture of a BAM Friction Test Apparatus (from the German Federal Institute for Materials Research and Testing, or “Bundesanstalt für Materialforschung”—“BAM”). In (a), a pyrotechnic composition is placed on a sliding plate in a shallow well. A porcelain pin is lowered into the well and a certain force is applied to the top. The sliding well plate will move in one direction and then another, and a fire/no-fire result will be observed (which can also be tested by pressure-sensing device that will detect gas production from an ignition). (b) A picture of an actual BAM Friction Test Apparatus (picture courtesy of UTEC Corporation, LLC, http://www.utec-corp.com/).

IMPACT SENSITIVITY

Impact ignition and sensitivity to impact refer to an inert, typically heavy and dense, mass colliding with the intended pyrotechnic mixture at some speed (usually dropped from a height to use gravity as the accelerator).

The generation of “hot spots” by the collision of a heavy, hard object with the surface of an explosive or pyrotechnic mixture appears to be the primary ignition “trigger” associated with impact sensitivity. Impact causes the compression of air pockets in the energetic material, leading to temperature rises due to adiabatic compression of the entrapped air. Another possible effect of impact is the ability of a given material to absorb the kinetic energy associated with impact and convert this energy into vibrational energy in a solid material sufficient to initiate a sequence of bond-breaking that leads to ignition.

The presence of grit or other hard material is important in impact-based ignition as the gritty material will rub against surfaces upon impact/compression to cause hot spots and “non-shock” initiation (Reynolds, et al. 2017). Some commercial explosives incorporate small glass “microspheres” that are specifically added to generate “hot spots” throughout the explosive and assist in achieving detonation of the material when a moderate detonation stimulus such as a blasting cap is inserted into the explosive material. Detonation of the blasting cap produces a number of sites of high temperature within the explosive near the detonator, through adiabatic compression of the microspheres, and the detonation then proceeds through the material, continuing to be assisted by the microspheres. The effectiveness of these spheres at sensitizing explosives provides substantial support for the “hot spot” theory of detonation initiation.

In the case of pyrotechnic and propellant materials, hot spot generation by impact will lead to ignition if a sufficient number of hot spots are created that exceed the ignition temperature of the material, and the heat that is thereby produced is sufficient to propagate the reaction through the remaining material. Table 7.4 shows impact sensitivity data for various compositions, while Table 7.5 shows a comparison of impact and friction data for a potassium perchlorate–zirconium (ZPP) composition.

It can be seen in Table 7.5 that friction sensitivity for this system is significantly affected by changes in the fuel–oxidizer ratio, while impact sensitivity shows only minor changes as the oxidizer–fuel ratio is varied. This tells us that while friction and impact ignition processes contain some similarities, there is *not* a one-to-one correlation between an increase in sensitivity to one type of ignition and an increase to another. This reinforces the notion that an individual suite of tests must be performed by the pyrotechnician on each new composition, and sensitivities for one type of ignition cannot simply be extrapolated from another.

TABLE 7.4
Impact Sensitivity Data for Some Pyrotechnic Compositions[a]

Composition	%by Weight	Impact Sensitivity (in.)	Comment
I. Magnesium (–200/+325 mesh)	75	3.75	Not friction-sensitive
Polytetrafluoroethylene	10		
Fluorelastomer	15		
II. Zirconium	65	10	Spark sensitivity <1 mJ
Iron oxide	25		
Diatomaceous earth	10		
VAAR binder	+1%		
III. Magnesium (–30/+50 mesh)	51	>10	Spark sensitivity >50 J (good), but friction sensitivity is 204 ft-lb^2/s(poor)
Sodium nitrate	42		
Epoxy/polysulfide binder	7		

[a] Aikman (1987).

TABLE 7.5
Friction and Impact Sensitivity for the "ZPP" System[a]

% Composition (Zr/ $KClO_4$)	Impact Sensitivity, Height of 50% Explosion (cm)	Friction Sensitivity (Pistol Load Up to Which Insensitive, Kgf)
10/90	115	36.0
20/80	106.5	36.0
30/70	106.25	36.0
40/60	90.0	14.4
50/50	92.5	10.8
60/40	99.1	5.4
70/30	92.5	4.8
80/20	103.0	3.6
90/10	94.0	2.0

Note: Impact sensitivity varies little with change in percent of Zr, while friction sensitivity does change 18-fold, becoming more sensitive as the percent of Zr is increased.

[a] Durgapal (1988).

There are two common types of impact sensitivity tests: a "hammer drop" test and a "ball drop" test. In the former case, a sample of material is placed on a flat surface and a heavy flat metal "hammer" is dropped from a specific height onto the material, and ignition is observed or not. In some cases, the material can be placed in a hollow tube with a cylinder or pin on top to focus the energy of the impact. As the hammer falls from a higher height, the hammer is moving faster when it impacts the material and more kinetic energy is transferred from the hammer to the energetic material, possibly inciting ignition. Figure 7.5 shows mock-up drawings of the hammer drop test setup and a BOE hammer impact test apparatus.

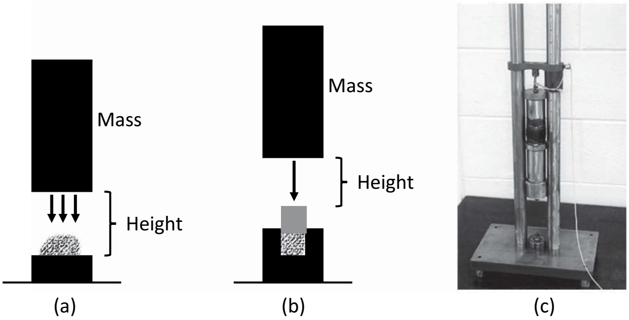


FIGURE 7.5 Mock-up drawings and a picture of a BOE (Bureau of Explosives) Impact Test Apparatus. (a) A hammer with a certain mass dropping from a certain height onto a flat plate with loose pyrotechnic material. The observer will record a fire/no-fire result. (b) A similar setup, except the loose pyrotechnic material is put into a cup holder with a cylinder pin placed on top which the hammer will strike, and the observer will again record a fire/no-fire result. (c) A picture of an actual BOE Impact Test Apparatus (picture courtesy: UTEC Corporation, LLC, http://www.utec-corp.com/).

The "ball drop" test was developed by the U.S. Army (U.S. Army Armament Research, Development, And Engineering Center 2011). In this test, 30 mg of the material in question is subjected to the impact from a falling 1 oz. steel ball. Like the hammer test, as the ball falls from a higher height, more kinetic energy comes with the ball that is transferred to the pyrotechnic.

When running a series of impact tests, such as the number of ignitions out of 10 trials, the same sample of material *cannot* be used again if it does not ignite the first time. The impact from the first trial will compress the material, and the impact sensitivity can change drastically depending on the bulk density of a particular pyrotechnic (logically, one might expect the impact sensitivity of pressed material to be less than that of a loose material although this may not always be true!). Mixtures should always be sensitivity-tested in the state that they are to be stored or used in.

THERMAL SENSITIVITY

Thermal Sensitivity Overview

Thermal sensitivity data is now primarily obtained using the thermal analysis method of differential scanning calorimetry, or DSC. Not only the best understood, thermal sensitivity is also the most reproducible of the various types of sensitivity tests, owing to the consistency of technical equipment and specific test conditions for the value that is obtained. Thermal sensitivity is the result of the chemistry that occurs in a given mixture upon heating, and it is relatively independent of factors such as homogeneity, particle size, and percent composition. It can be *very* dependent, however, on the addition or omission of a component in a particular composition, especially if that component plays a role in the initial exothermic reaction that occurs upon heating of the material. Even a very small amount of a contaminant, if reactive enough, can begin ignition for an entire composition before a more-pure mixture would have.

Ignition temperature measurements determine the minimum temperature at which a composition begins to react in a rapid, exothermic, self-propagating manner as a sample is heated. Such measurements are based on the exposure of the sample material to a continually increasing temperature, and the experimental method is affected to only a minor degree by factors such as blended grain size, degree of confinement, and even the testing method and heating rate that is employed. Ignition temperature is therefore a fairly reproducible value for a given pyrotechnic composition from laboratory to laboratory as well as from country to country. It appears that the reproducibility of ignition temperatures, for a specific energetic mixture, is usually within ±25°C from one study to another, regardless of the variables from study to study.

Thermal sensitivity gives an indication of the potential hazard represented by exposure of a given composition to elevated temperature during mixing, drying, and storage. Second, it gives the manufacturer an idea of ignition transfer problems that a given formulation is likely to present. For example, compositions that are difficult to ignite typically have high ignition temperatures of 500°C or more, while easy-to-light mixtures usually have ignition temperatures substantially lower in value. Many chlorate-based "stars," long valued by the fireworks industry for their ease of ignition and reliable propagation of burning, have ignition temperatures below 200°C. Their ease-of-ignition benefit during use in an end item is offset by their sensitivity to ignition during manufacturing, however. Some representative ignition temperatures are given in Table 7.6.

Many of the oxidizers used in pyrotechnic compositions melt at relatively low temperatures (Table 3.2), and melting of the oxidizer often precedes or coincides

TABLE 7.6
Ignition Temperatures (by DSC) of Some Pyrotechnic Compositions[a]

Composition		% by Weight	T_{ignition}(°C)	Use
I.	Potassium chlorate	42	193	Base mix for colored smokes (without dye)
	Sugar	28		
	Magnesium carbonate	30		
	Nitrocellulose binder	+3.4%		
II.	Red lead oxide	73.3	200	Delay mixture
	Silicon	18.4		
	Nitrocellulose	8.3		
III.	Potassium nitrate	10	334	Ignition mixture
	Barium chromate	65		
	Boron	21		
	VAAR binder	4		
IV.	Potassium nitrate	70.7	410	Ignition mixture
	Boron	23.7		
	Polyester binder	5.6		
V.	Sodium nitrate	49	502	Illuminant
	Magnesium (−20/+50 mesh)	40		
	Polyester binder	11		
VI.	Potassium perchlorate	20	587	White smoke
	Potassium nitrate	20		
	Aluminum	20		
	Zinc dust	40		
VII.	Red lead oxide	85	786	Delay mixture
	Silicon	15		
	Nitrocellulose binder	+1.8%		

Note: Compare to composition B above—the % nitrocellulose is the reason that the T_{ignition} is lowered.

[a] Aikman (1987).

with ignition of the oxidizer when mixed with an elemental fuel such as magnesium or boron. The melting process of a pure material can be detected by thermal analysis and typically appears as a sharp endotherm on the temperature/heat differential plot, or thermogram. Significant release of oxygen by the oxidizer is frequently associated with the onset of melting of the solid oxidizer material. A thermal analysis technique known as thermal gravimetric analysis, or "TG," which monitors any change in sample weight as a function of increasing temperature, can be used to study the release of oxygen by a sample of pure oxidizer, since the sample will become lighter in weight as oxygen gas is released on heating.

Metal fuels, in general, have higher melting points than most oxidizers, and the metal is often protected by a surface oxide coating that retards further oxidation of the metal as oxygen is released by the oxidizer upon heating of an oxidizer–fuel mixture. The oxide coating is shed as the metal fuel approaches its melting point, and fresh, active metal surface is exposed. Rapid oxidation usually follows. Hence, oxidizer–metal compositions frequently display ignition temperatures approaching the melting point of the metal, as shown in Table 6.4.

Organic compounds consisting of carbon, hydrogen, oxygen, and sometimes nitrogen—often used as fuels and binders in energetic mixtures—are typically characterized by decomposition temperatures in the 200°C–350°C range, temperatures which are often *lower* than the melting point of the oxidizer that is mixed with the fuel. The weakest chemical bonds in the organic molecules break, forming very reactive fragments: so-called "free radicals" since they have an unpaired electron available for bonding. These fragments are often quite susceptible to oxidation and are converted to carbon dioxide, carbon monoxide, and water by reaction with atmospheric oxygen or with oxygen released by the thermal decomposition of the solid oxidizer. Once the oxidizer begins to release oxygen, exothermic reactions should begin to quickly occur. This oxidation of the organic fragments releases heat, raising the overall temperature of the system. This temperature elevation then accelerates all of the decomposition reactions that are occurring. More heat is liberated and the overall process is sent into an upward spiral, leading to ignition and propagation of burning.

Thermal sensitivity therefore requires that a sample be heated to a temperature where two conditions are met:

1. The oxidizer reaches a temperature where sufficient evolution of oxygen occurs.
2. The fuel reaches a temperature where it is in a chemical state capable of reacting with the oxygen released by the oxidizer. For a metal or other elemental fuel, this will typically occur as the element approaches its melting point. For a carbon-based fuel, this will occur when the compound reaches its decomposition temperature (typically between 200°C and 350°C).

A mixture consisting of an oxidizer, metal fuel, and organic binder can therefore display interesting ignition temperature (and thermal sensitivity) behavior. At low percentages of binder, the heat released by the decomposition and oxidation of the binder is not sufficient to activate the metal fuel by raising the sample temperature to the metal's melting point. With higher binder percentages, the low-temperature reaction between oxidizer and binder may now be sufficient to activate the metal, leading to an ignition temperature several hundred degrees below the ignition temperature of a binary mixture of the same metal and oxidizer. The binder is not only providing mechanical strength and cohesion to the mixture but it may also thermally sensitize the mixture by providing a low-ignition-temperature fuel to the system. Several examples of this phenomenon are given in Tables 6.1 and 7.6.

DIVERGENT SENSITIVITY CHANGES

It is for the reason shown above that any change in an energetic formula must be watched carefully for sensitivity changes, both becoming more sensitive, as well as possibly becoming less sensitive. A mixture with 6% organic binder may have an ignition temperature considerably lower than the same mixture with only 2% binder, more thermally sensitive. But these minor changes may also affect the spark and friction sensitivity of energetic mixtures. For example, the addition of 4% diatomaceous earth (which can be a gritty material) as a diluent to slow the burn rate of a delay composition may significantly *enhance* the friction sensitivity of the mixture, as well as simultaneously *decrease* the spark sensitivity of the material. It is therefore important to fully reassess the sensitivities of a composition *anytime* that a change in formulation is made. It would go without saying, but it will be repeated, that one *must* re-evaluate sensitivity if a chemical substitution or replacement is made, such as the replacement of aluminum by magnesium–aluminum alloy. New sensitivity values should be determined, and the new or revised mixture must then be determined to be acceptable from a sensitivity point of view, before any large quantity of the new mixture is blended and processed.

It must also be realized that sensitivity measurements relate to the composition *as tested*. Grain size, extent of residual solvent, humidity, and time elapsed following mixing are among the factors that can affect sensitivity values. During the mixing process, it is possible that the protective oxide coating acquired by some fuels might be removed, exposing fresh fuel surface that might be more sensitive to a spark or other stimulus. Once mixing is finished, the fuel gradually reacquires a protective coating, and its sensitivity is likely to change, becoming less spark-sensitive as this reoxidation process occurs.

Spark sensitivity data for a calcium chromate–boron composition, measured as a function of blending time in a rotating "ball mill," are shown in Table 7.7 (Wang and Hall 1988). These figures clearly show that sensitivity can change during the manufacturing process and clearly indicate that the sensitivity of in-process mixtures can be significantly different than the measured sensitivity values on aged composition. In the Wang and Hall study, the composition is presumably undergoing a change in homogeneity, a reduction in component particle size, and a "polishing" of the boron particles as the boron oxide coating of the born particles is removed during mixing—making the composition more sensitive to spark. It can be assumed that there will be a rise in the spark sensitivity value (decrease in spark sensitivity) for the mixture following the ball milling operation as it ages and the boron surface re-oxidizes over time. The final spark sensitivity level observed when the composition stabilizes over time will be a reflection of the relative contributions of the various factors that are involved.

TABLE 7.7
Electrostatic Spark Sensitivity vs. Mixing Time in a Ball Mill

Time of Ball Mill Treatment (h)	Spark Sensitivity (mJ)
0	>750
0.5	529
1	270
5	77
50	27

Notes: The composition is calcium chromate (80) and boron (20). These values were taken immediately upon removal from the ball mill with minimal exposure time to air.

SHOCK SENSITIVITY: A BRIEF NOTE

As discussed early in this book, explosives are another category of energetic materials that are intended to rapidly release large amounts of heat and energy and often do so through detonation, as opposed to extremely rapid combustion “deflagration.” Many high explosives (such as RDX, HMX, and PETN) are intended to only perform under the specific circumstance of shock ignition and will only mildly burn when exposed to a routine flame or heat source. In ignition, a supersonic blast front essentially “shatters” molecules into pieces to react, as opposed to the thermal ignition behaviors discussed previously. This supersonic blast front is often called a “shock front” and many high-explosives will only act as such if they receive a substantial shock front to initiate their effect, furthering the shock front into the unreacted material.

Therefore, high explosives under test are often evaluated as to whether they will detonate with a certain shock impetus, often from that of a detonator “blasting cap,” or just “cap.” A material is said to be “cap sensitive” if it detonates with a specific blasting cap. These blasting caps are filled with a powerful pyrotechnic such as mercury fulminate [$Hg(ONC)_2$] or lead azide [$Pb(N_3)_2$] (often called “primary explosives”) that, once electrically ignited, provide an initial shockwave intended to initiate the main explosive material (sometimes called the “secondary explosive”). The United Nations has published a standard cap sensitivity test, with a standard cap as the initiator in standard test conditions (United Nations 2009). High-speed video, witness electronics, and a physical “witness plate” underneath the incident explosive material can be reviewed to determine whether a detonation took place and the speed of the shockwave involved.

Common pyrotechnics for civilian, commercial, and even military use rarely require blasting caps for initiation (although they will almost certainly ignite if used!), instead opting for thermal, electrical, or physical means of ignition. Testing a pyrotechnic against a blasting cap to determine “cap sensitivity” tells as much about the sensitivity as testing a dinner plate with a sledgehammer: quite a bit of overkill! Cap sensitivity is much more common to high explosives for blasting or military applications.

The chemistry of explosives and their engineering, shock sensitivity, and detonation physics can be intensely studied in numerous other texts (Akhavan 2004) (Kohler and Meyer 1993) (Cooper 1996).

REDESIGNING A COMPOSITION FOR SENSITIVITY CONSIDERATIONS

If a composition is determined to be too sensitive for safe production, storage, transport, and/or use, the only alternative is to redesign the composition in an effort to find a replacement material that works as well as the "bad" composition but is one that can be produced and used safely in manufacturing. This can be an expensive proposition, since the new mix must go through a complete qualification and approval process to ensure performance. But, there is often little choice but to proceed with finding a replacement should sensitive values suggest a high probably of ignition incidents should the "bad" material be produced and used in manufacturing operations.

An example of such a situation involved an ignition mixture for a smoke device. The initial ignition composition consisted of:

Component	Weight Ratio
Barium chromate, $BaCrO_4$	65
Potassium nitrate, KNO_3	10
Boron	21
VAAR[a] binder	4

[a] VAAR, vinyl alcohol acetate resin.

Test	Result
Spark sensitivity	0.107 J
Impact sensitivity	3.75 in. (BoE apparatus)
Friction sensitivity	86 ft-lb^2/s (rotary friction)
Ignition temperature	334°C

Sensitivity testing of this material yielded the following results (Aikman 1987):

While the ignition temperature was in the "moderate" range, impact, friction, and spark sensitivity values for this material were all of concern. Given that the mixture was being used to ignite colored smoke composition containing potassium chlorate and sugar (ignition temperature under 200°C), a milder ignition mixture with much better sensitivity properties could be used. The replacement material was as tabulated:

Component	Weight Ratio
Potassium nitrate, KNO_3	49
Silicon	36
Charcoal	6
Stearic acid (lubricant)	5
Nitrocellulose binder	4

In this material, the spark-sensitive fuel boron has been replaced by silicon, and the wax-like stearic acid has been added to reduce friction and impact sensitivity. This material showed the following sensitivity values:

Test	Result
Spark sensitivity	>50 J
Impact sensitivity	>10 in.
Friction sensitivity	47,114 ft-lb^2/s
Ignition temperature	>330°C

A much safer material to use in the manufacturing process was developed, with no loss of reliability or performance for the end item when fully tested and qualified for use.

PYROTECHNIC SENSITIVITY: SUMMARY

Unfortunately, there is no such thing as a fixed or constant value for the ignition sensitivity of an energetic mixture, whether the stimulus is spark, impact, friction, or elevated temperature. Sensitivity can vary greatly due to factors such as particle size, grain size, homogeneity, aging, moisture content, and the type of energy impinging upon the material. The only safe thing to do is consider *all* energetic materials to be sensitive to *all* types of ignition stimuli, at least until a history of safety has been established for a given material. Change one variable in the whole equation, however, and it's back to square one—the material must be considered highly sensitive until it has been thoroughly retested for sensitivity to all modes of energy input.

A general "rule of thumb" when talking about sensitivity is illustrated in Table 7.8, showing where general terms of "high," "moderate," and "comparably insensitive" can be applied to specific data on ignition temperature, spark sensitivity, and impact sensitivity. However, no standard set of terms or sensitivity equivalents has yet been agreed upon in the pyrotechnics community, and this table should be used only as a general starting point and not a scientific standard. A key distinction between this table and the one originally proposed by Bailey (Bailey 1992) is the raising of the spark sensitivity level for "high" classification from 1 to 100 mJ. This has been done to include any composition that tests near human spark energy levels of 10–15 mJ into the "high" category, with a safety factor of approximately 6–7 added in.

TABLE 7.8
A Proposal for Sensitivity Value Classification[a]

Term	Ignition Temp(°C)	Spark(mJ)	Impact Height, in.(BoE Apparatus)
High sensitivity	<200	<100	<3.75
Moderate sensitivity	200–400	100–450	3.75–10
Comparatively insensitive	>400	>450	>10

Note: Values have been modified from the proposal in Bailey et al., which is an *excellent* paper for discussion/friendly debate purposes.

[a] Bailey (1992).

The best way to use sensitivity data is in a comparative manner. For example, we know that zirconium potassium perchlorate (ZPP) is very spark-sensitive and has been involved in safety incidents during manufacture that have been traced to spark initiation. If a new composition is developed that has the same spark sensitivity as ZPP (measured on the same test apparatus), we know that we are going to have to be *very* careful working with the new material, and we should make every effort to modify the composition to make it less sensitive if the requisite performance can be maintained.

8 Heat Compositions

Ignition Mixes, Delays, and Thermites

BURNING RED STAR: Colors are produced in burning pyrotechnic compositions by the use of specific chemical elements and began to find wide use in pyrotechnics by the beginning of the 19th century. Strontium, as strontium nitrate or strontium carbonate, will impart a beautiful red color to the flame of a burning pyrotechnic material. The effect is used for entertainment and for emergency signaling in both military and civilian applications.

One thing all energetic materials have in common is the fact that they are exothermic and self-propagating in their conversion from starting materials to reaction products. Once an initial ignition stimulus is successfully applied, burning continues without the need for any additional external energy, and heat is produced along with any desired effect: smoke, sound, color, gas products, etc. However, in some compositions, it is the heat itself, and the work that it can do, that is the primary purpose of the mixture.

HEAT PRODUCTION

All pyrotechnic compositions evolve heat upon ignition, and this release of energy can be used to produce color, motion, smoke, and noise. There are applications as well for the chemically produced heat itself and the hot products from these reactions, and these will be addressed in this chapter.

The use of incendiary[1] mixtures in warfare can be traced back to ancient times, when fireballs provided an effective means of assaulting well-fortified castles or wooden ships. The so-called "Greek fire" was an incendiary weapon originally employed by the Byzantine Empire in the 7th century and thought to consist of a petroleum base with possibly sulfur, potassium nitrate, and/or other resins (though it was a closely held secret, and therefore the exact formulation is unknown). More modern naval warfare was revolutionized by the use of propelled objects (such as cannon balls) to attack wooden ships, and much effort was put into improving the heat output, range, portability, and accuracy of these thermal weapons.

As both weaponry and the use of explosives for blasting developed, the need for safe, reliable ways to ignite these devices became obvious, and the concepts of an ignition fuse and a pyrotechnic "delay" emerged. Therefore, heat-based ignition systems and preceding ignition-delay systems have been closely intertwined since their first use: The pyrotechnician must not only be able to reliably ignite compositions but must also know to stay away when the main composition is ignited, requiring a delay.

IGNITERS AND DELAYS: TERMINOLOGY

A variety of terms are used for materials that either ignite or provide a delay period between ignition of a device and the production of the main explosive or pyrotechnic effect. These include the following:

1. *Fuse:* A train of pyrotechnic composition (usually black powder), often covering, or covered with, inexpensive materials such as twine, thread, or twisted paper, as well as a waterproofing material. Fuses are lit by a safety match or other hot object and provide a time delay to permit the person igniting the device to retreat to a safe distance. This term should not be confused with "fuze," which is a device used to initiate a military explosive device such as a bomb.
2. *Electric Match* (*often inaccurately referred to as a "squib," see #7 below*)*:* A device containing a thin metal wire, termed a bridgewire, that is coated with a dab of heat-sensitive pyrotechnic composition. An electric current is passed through the bridgewire, using a wire circuit, and a temperature rise occurs in the bridgewire that ignites the small dab of match composition. A burst of flame is produced that ignites a section of fuse or a charge of pyrotechnic composition. Electric match compositions sometimes contain potassium chlorate (usefully for its low ignition temperatures). Lead mononitroresorcinate

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[1] Incendiary, from the Latin *incendere*, "to set fire to."

[LMNR—$Pb(C_6H_3NO_4)_2$] is also included in some electric match mixtures; LMNR is an "initiating explosive" and substantially hazardous to work with but is reliably sensitive to ignition and provides a very useful heat "punch" for ignition. Several e-match formulas are listed in Table 8.1.

3. *First Fire:* An easily-ignited composition that is pressed, coated, or otherwise placed in limited quantity on top of the main pyrotechnic mixture. The first fire is reliably ignited by a fuse or electric match, and the flame that is produced, in addition to the hot residue left sitting on top, then ignites the main charge. Black powder, moistened with water containing a binder such as dextrine, is often used in the fireworks industry as a first fire and also helps secure the fuse to the item. First fires are often referred to as "primes"— a term similar to another with a distinct meaning (see #5 below).
4. *Delay Composition:* A general term for a mixture that burns at a reliable, reproducible rate, thereby providing a time delay between activation of a device and production of the main effect. A fuse containing a core of fine-grain black powder is an example of a delay. Highly reproducible delay mixtures are needed for military applications, and much research effort has been put into developing reliable compositions that are effective under a wide range of temperature and pressure.
5. *Primer* (*a common version is the "percussion primer"*)*:* A term for the device used to ignite smokeless powder in small arms ammunition or other propellant applications. An impact-sensitive composition is typically used, think about common pistol ammunition. When struck by a metal firing pin, a primer emits a burst of flame and hot particulates capable of rapidly igniting the propellant charge. Several typical primer mixtures are given in Table 8.2.
6. *Friction Igniter:* A truly "self-contained" fully engineered device should be ignitable without the need for a safety match, battery, or other type of external energy source. Highway flares (fusees) – other types of distress signals, some military devices, and even common household matches – use a friction ignition system. For example, the fusee uses a two-part igniter: when

TABLE 8.1
Electric Match Compositions[a]

Component		Formula	% by Weight
I.	Potassium chlorate	$KClO_3$	8.5
	Lead mononitroresorcinate	$Pb(C_6H_3NO_4)_2$	76.5
	Nitrocellulose	–	15
II.	Potassium chlorate	$KClO_3$	55
	Lead thiocyanate	$Pb(SCN)_2$	45
III.	Potassium perchlorate	$KClO_4$	66.6
	Titanium	Ti	33.4

[a] McIntyre (1980).

TABLE 8.2
Typical Primer Mixtures[a]

Component		Formula	% by Weight	Notes
I.	Potassium chlorate	$KClO_3$	45	Stab primer
	Lead thiocyanate	$Pb(SCN)_2$	33	
	Antimony sulfide	Sb_2S_3	22	
II.	Potassium chlorate	$KClO_3$	33	Stab primer
	Antimony sulfide	Sb_2S_3	33	
	Lead azide	$Pb(N_3)_2$	29	
	Carborundum	SiC	5	
III.	Potassium chlorate	$KClO_3$	50	Percussion primer
	Lead peroxide	PbO_2	25	
	Antimony sulfide	Sb_2S_3	20	
	Trinitrotoluene	$C_7H_5N_3O_6$	5	
IV.	Potassium perchlorate	$KClO_4$	50	"ZPP"
	Zirconium	Zr	50	Percussion primer

[a] McIntyre (1980).

the two surfaces are rubbed together, a flame is produced and the main composition is ignited. Typically, the scratcher portion of these devices contains red phosphorus and an abrasive, gritty material like pumice, and the match head mixture contains potassium chlorate ($KClO_3$) and a good fuel/binder material. Two example friction igniter systems, with their main composition, are given in Table 8.3.

7. *Squib:* A device containing an electric match (see #2 above) as well as a small quantity of pyrotechnic output charge, typically black powder. The electric match ignites the black powder, which in turn produces a flame and sparks to ignite propellant or other pyrotechnic composition. The term "squib" had been used to mean any device used to ignite any other pyrotechnic composition, which led to electric matches being called "squibs." However, the preferred use of "squib" among pyrotechnicians is a device that incorporates an electric match and an additional pyrotechnic or "base charge" used to ignite the main pyrotechnic (Kosanke, et al. 2012).
8. *Igniter*: A general term for devices used to initiate pyrotechnic or propellant systems. Igniters are typically initiated electrically and produce a high-temperature output consisting of flame and hot particulates. Some common ignition and first-fire compositions are given in Table 8.4.
9. *Detonator:* An explosive device used to produce a detonation in a high explosive material. Detonators typically contain an ignition mixture, a sensitive "primary" explosive that detonates from the ignition stimulus, and a "secondary" high explosive output charge that is taken to detonation by

TABLE 8.3
Friction Igniter Mixtures

Component	Formula	% by Weight
I. Shidlovskiy Composition[a]		
Potassium chlorate	$KClO_3$	60
Antimony sulfide	Sb_2S_3	30
Resin	–	10
Striker		
Red phosphorous	P	56
Ground glass	SiO_2	24
Phenol/formaldehyde resin	$(C_{13}H_{12}O_2)_7$	20
II. McLain Composition[b]		
Shellac	–	40
Strontium nitrate	$Sr(NO_3)_2$	3
Quartz	SiO_2	6
Charcoal	C	2
Potassium perchlorate	$KClO_4$	14
Potassium chlorate	$KClO_3$	28
Wood flour	–	5
Marble dust	$CaCO_3$	2
Striker		
Lacquer	–	61
Pumice	–	2.2
Red phosphorous	P	26
Butyl acetate	$C_6H_{12}O_2$	10.8

[a] Shidlovskiy (1964).

[b] McLain (1980).

the shock from the detonation of the small amount of "primary" explosive [which is often lead azide, $Pb(N_3)_2$]. This secondary detonation can then be used to initiate a bulk secondary (or "tertiary") main charge. Detonators are used with *explosive* devices, but they are not typical components of propellant or pyrotechnic systems as they are significant overkill for ignition.

10. *Thermite:* A mixture of a metal fuel, typically aluminum powder, and a metal oxide to react forming aluminum oxide and molten metal (from what used to be the metal oxide). The classic thermite composition is between aluminum and iron oxide although other metal fuels (such as magnesium) can be used, along with other oxidizers (such as copper oxide or manganese dioxide).

IGNITION COMPOSITIONS AND FIRST FIRES

Compositions with high ignition temperatures (i.e., above 600°C) can be difficult to ignite using solely the "spit" from a black powder fuse or similar mild ignition stimulus. For black powder, the flame temperature is estimated to be 1,500°C, but the burning ash

TABLE 8.4
Igniter and First-Fire Formulations

Mixture	Component	Formula	% by Weight	Note
I. (Shidlovskiy 1964)	Barium peroxide	BaO_2	80	Solid BaO particles aid in ignition
	Magnesium	Mg	18	
	Binder	–	2	
II. (McIntyre 1980)	Iron oxide	Fe_2O_3	25	A1A mixture, a "gasless" igniter
	Zirconium	Zr	65	
	Diatomaceous earth	–	10	
III. (Shidlovskiy 1964)	Black powder	KNO_3/S/C	75	
	Potassium nitrate	KNO_3	12	
	Zirconium	Zr	13	
IV. (Shidlovskiy 1964)	Potassium nitrate	KNO_3	71	B/KNO_3 mixture
	Boron	B	24	
	Rubber	–	5	
V. (McIntyre 1980)	Red lead oxide	Pb_3O_4	50	
	Titanium	Ti	25	
	Silicon	Si	25	
VI. (McIntyre 1980)	Sodium nitrate	$NaNO_3$	47	
	Sugar	$C_{12}H_{22}O_{11}$	47	
	Charcoal	C	6	
VII. (Shidlovskiy 1964)	Barium peroxide	BaO_2	88	Thermite-style igniter
	Magnesium	Mg	12	
VIII. (Lake 1982)	Lead styphnate/lead 2,4,6-trinitroresorcinate	$C_6HN_3O_8Pb$	53	"PA 101" mixture used for percussion primers
	Barium nitrate	$Ba(NO_3)_2$	22	
	Tetracene	$C_{18}H_{12}$	5	
	Aluminum	Al	10	
	Antimony sulfide	Sb_2S_3	10	

"spit" product may not be sufficient enough hot material to make contact with transfer heat and finally ignite the main composition at the ignition temperature. In such situations, an initial charge of a more-readily-ignitable material, called a "first fire," is frequently used. The requirements for such a mixture include (Shidlovskiy 1964):

1. *Reliable ignitibility* for the first fire itself from a small thermal impulse such as a fuse, black powder, or a primer, or alternatively from a percussion/impact primer. The ignition temperature of a "first fire" should be 500°C or less for best results.
2. A *high reaction and flame temperature* should be attained for the mixture, well above the ignition temperature of the main composition. Metal fuels are usually used when *high* reaction temperatures are needed.
3. *Forming hot products* such as a hot liquid, slag, and/or solid particulates are preferred. Such slag will provide considerable surface contact with the main composition, transferring heat and facilitating ignition. The production of hot gas will usually produce good ignition behavior on the ground, but reliability may deteriorate at higher altitudes. Liquid and solid products provide better bulk heat capacity and heat transfer to aid ignition under these conditions.

A somewhat slower-burning ignition mixture is often preferred over a more rapid one, especially preferred over an explosive one. The shattering effect from an over-energetic ignition composition can cause the surface one is trying to light to crumble or scatter and thus yield ignition failures. The slower release of energy allows for better heat transfer to the main composition. Also, most "first fires" are pressed into place or added as moist pastes (that harden on drying), rather than used as faster-burning loose powders. Obviously, though, when you are igniting a device that must function very quickly (such as an air bag system), a very fast and energetic ignition material will be required. Then it is up to the engineer to figure how to "harness" the output from the energetic ignition material and still achieve high reliability in the end item.

The pyrotechnic engineer must balance the need for speed in the overall ignition process against possible explosive behavior from the ignition composition. To achieve this, potassium nitrate—a "moderate" oxidizer—is frequently used in ignition compositions and first fires. Compositions made with this oxidizer tend to have low ignition temperatures (typically below 500°C), and yet the mixtures are reasonably safe to prepare, to store, and to use in production. In addition, they tend to be a bit less explosive in their output than potassium perchlorate compositions blended with the same fuel. Potassium chlorate formulations also tend to have low ignition temperatures, but they are considerably more hygroscopic, sensitive, explosive, and hazardous, and thus are not widely used. Table 8.4 illustrates a range of ignition compositions.

Potassium nitrate mixed with charcoal can be used for ignition, as can black powder (the aforementioned mixture but with sulfur added) worked into a paste with water and a little dextrine. Shidlovskiy reports that the following composition

KNO_3	75
Mg	15
Iditol	10 (iditol is a phenol/formaldehyde resin)

works well as an igniter mixture (Shidlovskiy 1964); the solid magnesium oxide (MgO) residue aids in igniting the main composition and the resin helps to waterproof the magnesium.

Boron mixed with potassium nitrate is a frequently used, fast, effective igniter mixture, known in the industry as $BKNO_3$—“bee kay en oh three.” The boron must be watched closely for particle size and oxidation (particularly from exposure to moisture), and mixtures in the 70/30 potassium nitrate/boron range are quite energetic in output (known to deflagrate) and may be spark sensitive in manufacturing and handling (Charsley 1986).

The “ultimate” ignition compositions in use at the present time are materials containing an oxidizer blended with zirconium metal as the fuel. One such composition is a blend of iron(III) oxide with zirconium metal and diatomaceous earth (mostly silicon dioxide), commonly known as “A1A” ignition mixture. Even more energetic and faster burning is the ignition composition blended from zirconium and potassium perchlorate, known as “ZPP” (Durgapal 1988).

The zirconium-based ignition compositions tend to produce flame temperatures and hot particulate products in excess of 4,000 and even up to 5,000°C. Due to the extreme electrostatic spark sensitivity of fine zirconium and its pyrotechnic compositions, these materials must be handled under very controlled manufacturing conditions, and worked in a damp state whenever possible, with a full static protection program in place. Limited quantities of material, appropriate Personal Protective Equipment (PPE), remote mixing, and barricading for workers, must also be considered under the Process Hazard Analysis (PHA) for operations involving zirconium. However, if you do need to light something really fast, zirconium may be the material that is needed for the job. Ignition compositions can be quite energetic—Table 8.5 lists a variety of current ignition formulations, along with their approximate flame temperatures (computed) at atmospheric pressure (De Yong and Valenta 1989).

DELAY COMPOSITIONS

The purpose of a delay composition should be obvious from the name: to provide a time delay between the ignition action to the device and the delivery of the main effect. Crude delays can be made from loose powder, but a compressed column is capable of much more reproducible performance (essential for mass production of devices). The burning rates of delay mixtures range from very fast (mm/ms) to slow (mm/s, a thousand times slower).

Black powder was the sole pyrotechnic delay mixture available for several centuries. The development and use of “safety fuse” containing a black powder core significantly improved the safety record of the blasting industry. However, the development of modern, long-range, high-altitude projectiles created a requirement for a new generation of delay mixtures. Black powder, under specified conditions, gives fairly reproducible burning rates at ground level. However, it produces a considerable quantity of gas upon ignition (approximately 50% of the reaction products are gaseous), and its burning rate will therefore show a significant dependence on external pressure (burning faster as the external pressure increases, noting Table 6.8). To overcome this pressure dependence, researchers set out to develop “gasless” delays mixtures that evolve heat and burn at reproducible rates with the formation of almost

TABLE 8.5
Flame Temperatures of Some Igniter Compositions[a]

Composition		% by Weight	Flame Temperature(°C)
A1A	Zirconium	65	4,400
	Iron(III) Oxide	25	
	Diatomaceous earth	10	
ZPP	Zirconium	46	4,400
	Potassium perchlorate	53	
	Graphite	1	
$BKNO_3$	Boron	24	3,000
	Potassium nitrate	71	
	Lamanac® binder	5	
MTV	Magnesium	54	2,300
	Teflon®	30	
	Viton®	16	
Black powder	Potassium nitrate	75	1,500
	Charcoal	15	
	Sulfur	10	

Notes: The flame temperatures are computed values at approximately 40 atm. ZPP is very dangerous to prepare and handle, thus not recommended.

[a] De Yong and Valenta (1989).

exclusively solid and liquid products. Such mixtures will be expected to show little, if any, variation of burning rate with pressure.

One could begin a development project for a new delay system by setting down the requirements for an "ideal" delay mixture (Military Pyrotechnic Series Part One, "Theory and Application" 1967):

1. *Stability*: The mixture should be stable during preparation and storage. Materials of low hygroscopicity (i.e., do not tend to pull moisture from the ambient area) must be used.
2. *Ignitability*: The mixture should be readily ignitable from a modest ignition stimulus.
3. *Consistency*: There must be minimum variation in the burning rate of the composition with changes in external temperature and pressure. The mixture must readily ignite and reliably burn at low temperature and pressure.
4. *Constancy*: There should be a minimum change in the burning rate with small percentage changes in the various ingredients.
5. *Reproducibility*: Reproducible burning rates must be achievable in manufacturing, both within one batch of composition as well as between batches made days and weeks apart.

6. *Safety*: The component chemicals should be low in toxicity and environmentally friendly.

The standard “gasless” delays—for the past 60 years—have been some combination of a metal oxide or chromate (CrO_4^{2-}) oxidizer with an elemental fuel. The fuels are generally metals or high heat-producing nonmetallic elements such as silicon or boron. If an organic binder (e.g., nitrocellulose) is used, the resulting mixture will be “low gas” rather than “gasless,” due to the carbon dioxide (CO_2), carbon monoxide (CO), and nitrogen (N_2) that will form upon combustion of the binder. If a truly “gasless” mixture is required, leave out all organic materials!

THERMODYNAMICS AND DELAY COMPOSITIONS

If a fast burning rate is desired, a metallic fuel with high heat output per gram should be selected, together with an oxidizer of relatively low decomposition temperature. The oxidizer should also have a minimally endothermic—or even better, exothermic—heat of decomposition. For slower delay mixtures, metals with less heat output per gram should be selected, and oxidizers with higher decomposition temperatures and more endothermic heats of decomposition should be chosen. By varying the oxidizer and fuel, as well as the ratio of oxidizer-to-fuel, it is possible to create delay compositions with a wide range of burning rates. Table 8.6 lists some representative delay mixtures.

TABLE 8.6
Typical Delay Compositions[a]

Component	Formula	% by Weight	Burning Rate(cm/s)
I. Red lead oxide	Pb_3O_4	85	1.7 (10.6 mL/g of gas)
Silicon	Si	15	
Nitrocellulose/acetone	–	1.8	
II. Barium chromate	$BaCrO_4$	90	5.1 (3.1 mL/g of gas)
Boron	B	10	
III. Barium chromate	$BaCrO_4$	40	Burn rate not reported (4.3 mL/g of gas)
Potassium perchlorate	$KClO_4$	10	
Tungsten	W	50	
IV. Lead chromate	$PbCrO_4$	37	0.30 (18.3 mL/g of gas)
Barium chromate	$BaCrO_4$	30	
Manganese	Mn	33	
V. Barium chromate	$BaCrO_4$	80	0.16 (0.7 mL/g of gas)
Zirconium/nickel alloy (50/50)	Zr-Ni	17	
Potassium perchlorate	$KClO_4$	3	

[a] McIntyre (1980).

Using this approach, compositions with lead chromate (melting point 844°C) as the oxidizer would be expected to produce faster burning mixtures than those with barium chromate (which has a higher melting/decomposition point, ca. 1,400°C). Similarly, barium peroxide (melting point 450°C) mixtures should react more quickly than iron oxide (Fe_2O_3, melting point 1,565°C) mixtures. For fuels, boron (heat of combustion = 14.0 kcal/g) and aluminum (8.4 kcal/g) should form quicker delay compositions than tungsten (1.1 kcal/g) or iron (1.8 kcal/g). Tables 3.2, 3.4, and 3.5 can be used to estimate the *relative* burning rates of various delay candidates. Again, for high reactivity, look for low melting points, exothermic or minimally endothermic heat of decomposition (in the oxidizer), and high heat of combustion (in the fuel). For lower reactivity/speed, the opposite properties would be pursued.

STOICHIOMETRY AND DELAY COMPOSITIONS

The ratio of oxidizer to fuel can be altered for a given binary mixture to achieve substantial changes in the rate of burning. The fastest burning rate would be expected, chemically, to correspond to an oxidizer–fuel ratio near the stoichiometric point, with neither component present in excess. Data have been published for the barium chromate/boron system. Table 8.7 gives the burn time and heat output per gram for this system (Military Pyrotechnic Series Part One, "Theory and Application" 1967).

McLain has proposed that the maximum in performance, centered at approximately 15% boron by weight, indicates that the principal pyrotechnic reaction for the $BaCrO_4$/B system is

TABLE 8.7
The Barium Chromate/Boron System: Effect of % Boron on Burning Time[a]

% Boron	Average Burning Time(s/g)	Heat of Reaction(cal/g)
3	3.55	278
5	0.51	420
7	0.33	453
10	0.24	515
13	0.21	556
15	0.20	551
17	0.21	543
21	0.22	526
25	0.27	497
30	0.36	473
35	0.64	446
40	1.53	399
45	3.86	364

[a] Military Pyrotechnic Series Part One, "Theory and Application" (1967).

$$4B + BaCrO_4 \rightarrow 4BO + Ba + Cr \quad (8.1)$$

Although B_2O_3 is the *expected* oxidation product from boron in a room temperature situation, the lower oxide, BO, appears to be more stable at high reaction temperatures of the burning delay mixture (McLain 1980).

In practice, it has been observed in numerous systems that using a percentage of fuel in excess of the stoichiometric amount increases the burning rate for many delay mixtures, presumably through increased thermal conductivity for the composition (since most of the fuels used in delay mixtures are significantly better thermal conductors than the oxidizers). The propagation of burning is enhanced by the better heat transfer resulting from the additional fuel, especially in the absence of substantial quantities of hot gas to aid in the propagation of burning. Air oxidation of the excess fuel can also contribute additional heat to increase the reaction rate *if* the burning composition is exposed to the atmosphere.

The rate of burning of ternary (three-component) mixtures can similarly be affected by varying the percentages of the components; Table 8.8 presents data for this type of delay composition. In this study, a decrease in the burning (in cm/s) is observed as the metal percentage is lowered (giving poorer thermal conductivity) and the percentage of higher melting oxidizer ($BaCrO_4$) is increased at the expense of the lower melting, more reactive lead chromate, $PbCrO_4$.

Table 8.9 illustrates this same concept for the molybdenum/barium chromate/potassium perchlorate system. Here, $KClO_4$ is the better oxidizer, and more perchlorate by weight percentage shows faster burn rates. Another interesting study on this

TABLE 8.8
A Ternary Delay Mixture: The $PbCrO_4/BaCrO_4/Mn$ System[a]

Mixture	% Mn	% Lead Chromate	% Barium Chromate	Burning Rate(cm/s)
I.	44	53	3	0.69
II.	39	47	14	0.44
III.	37	43	20	0.29
IV.	33	36	31	0.19

[a] McLain (1980); Ellern (1968).

TABLE 8.9
The $BaCrO_4/KClO_4/Mo$ System[a]

Mixture	% Barium Chromate	% Potassium Perchlorate	% Molybdenum	Burning Rate(cm/s)
I.	10	10	80	25.4
II.	40	5	55	1.3
III.	55	10	35	0.42
IV.	65	5	30	0.14

[a] McLain (1980); Ellern (1968).

system showed that even when the excess metal in the system is inert silver powder[2], rather than excess molybdenum, the burn rate is still enhanced, indicating that the enhanced thermal conductivity due to the excess metal is indeed a significant factor (Rajendran 1989).

Contrary to the behavior expected for "gassy" mixtures, the rate of burning for gasless compositions is expected to *increase* (in units of grams reacting per second) as the *consolidation pressure* is increased. "Gasless" delays propagate via heat transfer down the column of pyrotechnic material, and the thermal conductivity of the mixture plays a significant role. As the density of the mixture increases due to the increased loading pressure, the components are pressed closer together and better heat transfer occurs. Table 4.7 presented data for the barium chromate/boron system, showing the modest rate increase (in g/s) that occurs as the loading pressure is raised. When significant gas products are produced, propagation of burning is enhanced by the movement/diffusion of the hot gaseous products into the unreacted material. In this case, high loading pressures block the penetration of the hot gases into the unreacted material, thereby decreasing the rate of heat transfer, and a decrease in burn rate may be observed.

"GREEN PYROTECHNICS" FOR DELAY SYSTEMS

The obvious 21st-century problem with the standard delay mixtures that have been in use for over 60 years is the fact that the oxidizers tend to contain blends of lead, hexavalent chromium (Cr with a +6 primary valence, or oxidation state), and barium. These are materials that do not meet several of the stated criteria for "green" pyrotechnics, the greatest of which is toxicity to humans and animals. One major issue with finding replacements for these "standard" delay compositions is the fact that we have a long history of manufacturing the standard compositions, and the effects of changes in particle size, percent composition, homogeneity, and moisture content are fairly well-known and can be used to "dial in" an appropriate delay. With new delay compositions based on different chemicals, the pyrotechnic scientist must go through the learning curve all over again to acquire knowledge of the "art" of producing these new compositions to achieve reproducible performance. Delay systems like iron(III) oxide with silicon or boron meet many of the 21st-century requirements, but their reproducibility in manufacturing and long-term storage stability are still being verified (Elischer 1986).

One possible replacement for chromate salts could be sulfate salts, such as barium sulfate ($BaSO_4$) or calcium sulfate ($CaSO_4$). Some studies of silicon-fueled/sulfate-oxidized delay systems have been reported, showing some notable differences between the cations (Tichapondwa, et al. 2016).

It is also possible that more use will be made of electronic delays containing no pyrotechnic component, particularly in more sophisticated devices. These electronic delays should provide higher precision and avoid the manufacturing variability that is inherent with the production of pyrotechnic devices. Delays of this type have already been introduced in commercial blasting detonators to achieve improved blasting results via precise delay intervals (Persson, et al. 1994). Notably, in the blasting industry, electronic delays have been shown to provide more accurate timing, more efficient explosive results, and costs savings over so-called "chemical delays" (Cardu, et al. 2013).

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[2] Silver itself is not "inert" in the classical chemical sense, but, in pyrotechnic reactions, very little silver will react to be oxidized as a normal fuel would be. It therefore it plays little role in heat generation, only heat transfer.

THERMITE AND THERMATE MIXTURES

Thermites are mixtures that produce a high heat concentration upon reaction, usually in the form of molten metal reaction products. Thermite compositions contain a metal oxide as the oxidizer and a metal—usually aluminum—as the fuel, although other active metals may be used. Thermite reactions are also called "Goldschmidt reactions" owing to the discoverer, German chemist Johann Wilhelm Goldschmidt, in the late 19th century (Kosanke, et al. 2012).

The classic thermite mixtures—often just referred to as "red thermite" or "black thermite" even though it is a class of mixtures, and not a mixture itself—is a combination of "red" iron(III) oxide or "black" iron (II,III) oxide and aluminum:

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe \tag{8.2}$$

$$3Fe_3O_4 + 8Al \rightarrow 4Al_2O_3 + 9Fe \tag{8.3}$$

Upon ignition, a thermite mixture will form aluminum oxide and the metal corresponding to the starting metal oxide, in this case iron. High reaction temperatures can be achieved in the absence of volatile materials, typically, values of 2,000°C–2,800°C (McLain 1980). A metal product such as iron that melts well below this reaction temperature (m.p. 1,535°C) will form as molten metal, showing the thermite's classic character and utility. Furthermore, iron has a high melting-to-boiling point range (1,535°C–2,800°C), allowing the metal to produce as liquid and not vaporize as a gas, producing excellent overall thermite composition behavior. Finally, since a minimum amount of gas is produced by these reactions, it enables the heat of reaction to concentrate in the solid and liquid products.

Thermite mixtures have found application as incendiary compositions and spot-welding mixtures (Jeffus 2017). They are also used for the intentional demolition of machinery and for the destruction of documents. Thermites are usually produced without a binder (or with a minimum of binder), because the gaseous products resulting from the combustion of the organic binder will carry away heat, cool the reaction, and possibly produce blast effects under confinement, scattering the molten metal intended to stay together in a single mass.

The particle size of the aluminum is important and should be somewhat coarse to prevent the reaction from being too rapid. Thermites tend to be quite safe to manufacture, and they are rather insensitive to most ignition stimuli. In fact, the major problem with most thermites is *getting* them to ignite, and a strong first fire is usually needed. Calorific data for a variety of aluminum thermite mixtures are given in Table 8.10, while Table 8.11 shows a comparison of calorific data for red iron oxide (Fe_2O_3) thermite mixtures with aluminum, magnesium, and titanium as the fuel.

TABLE 8.10
Calorific Data for Aluminum-Based Thermite Mixtures[a]

Oxidizers	Formula	% Active Oxygen by Weight	% Al by Weight in Thermite Mixture	$\Delta H_{reaction}$(kcal/g)
Silicon dioxide	SiO_2	53	37	0.56
Chromium (III) oxide	Cr_2O_3	32	26	0.60
Manganese dioxide	MnO_2	37	29	1.12
"Red" iron oxide	Fe_2O_3	30	25	0.93
"Black" iron oxide	Fe_3O_4	28	24	0.85
Cupric oxide	CuO	20	19	0.94
Lead oxide (red)	Pb_3O_4	9	10	0.47

[a] Shidlovskiy (1964).

Because thermites tend to be insensitive to ignition, a class of similar compositions dubbed "thermates" has been evaluated. Thermates are simply thermites with additional oxidizers added to aid in ignition for incendiary applications. Table 8.12 lists three thermate compositions, which all still include the iron oxide and aluminum thermite base, but with added oxidizers, fuels, and/or binders (Kosanke, et al. 2012). Note that different particle-sized aluminums can be used in the same composition, which can help dial-in the rate of reaction and production of a desired incendiary effect.

TABLE 8.11
Calorific Data for Red Iron Oxide-Based Thermite Mixtures[a]

Fuel	Formula	$\Delta H_{reaction}$(kcal/mol)
Aluminum	Al	101.8
Magnesium	Mg	78.1
Titanium	Ti	94.6

[a] Weiser, et al. (2010).

TABLE 8.12
Example Thermate Mixtures

Mixture	Fe_3O_4	Al (200 Mesh)	Al (−12/+140 Mesh)	Mg	S	$Ba(NO_3)_2$	KNO_3	Binder	Resin
Shidlovskiy[a]	21	13	–	12	–	44	6	4	–
Ellern-I (Ellern 1968)	44	9	16	–	2	29	–	–	–
Ellern-II (Ellern 1968)	51	3	19	–	–	22	–	–	5

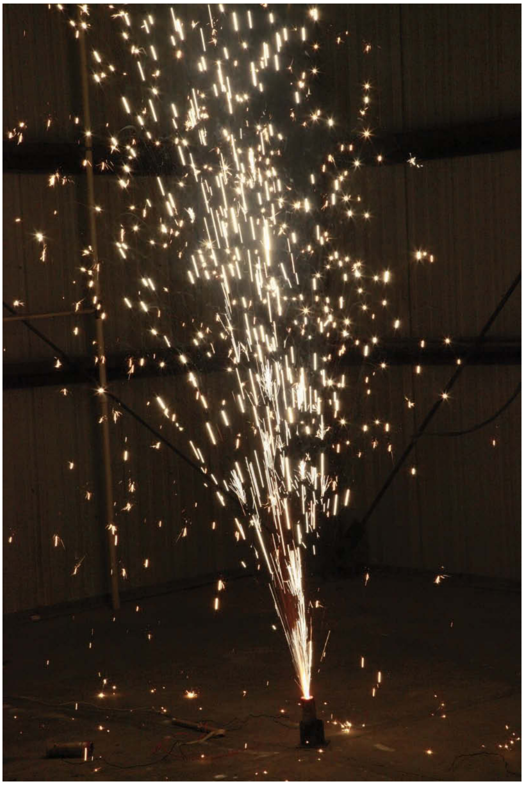
[a] Shidlovskiy (1964).

HEAT COMPOSITIONS: SUMMARY

To be of practical use, pyrotechnic compositions need to be reliably ignited, in a reliable manner. To this requirement, ignition compositions are invaluable in utilizing their heat to ignite the main pyrotechnic, and delay compositions are equally invaluable to engineer exactly the main pyrotechnic to be ignited as desired. Both ignition and delay compositions need to be reliable for their intended use and can be manufactured using pyrotechnic principles to perform in a variety of ways depending on the need of the pyrotechnician.

9 Propellants

A Brief Overview



TITANIUM SPARKS: A titanium fountain uses relatively coarse titanium particles blended into a moderately fast-burning pyrotechnic composition to produce a beautiful spray of white sparks. This type of "fountain" effect is widely used in the fireworks industry as well as in theatrical pyrotechnical articles (special effects) for stage presentations.

The production of hot gas to lift and move objects, using a pyrotechnic system, began with the development of black powder centuries ago and has advanced with new chemicals and systems in the modern era. From the smallest bottle rocket to a NASA launch vehicle, pyrotechnic propellants are a class of their own in the study of energetic materials, with any number of texts focusing on their chemistry and engineering.

PROPELLANTS: AN INTRODUCTION

The production of hot gas to lift and move objects, using a pyrotechnic system, began with the development of black powder and the rapid generation of carbon dioxide, nitrogen, and other gases. Rockets with black powder propellant were in use in Italy in the 14th century, and cannons were developed at about the same time (Parington 1960). The development of aerial fireworks, along with muskets and other firearms, was a logical extension of cannon technology. In the 1800s, nitrocellulose (the original "smokeless powder") was developed, followed by double-based nitrocellulose/nitroglycerin propellants and further advancements in the 1900s and today (Kosanke, et al. 2012).

Propellants are briefly discussed in this chapter, with emphasis on those with a composition similar to traditional pyrotechnic formulations—oxidizer, fuel, and binder. Propellants can also be formulated from energetic materials that more closely resemble high explosives than pyrotechnics, with nitrocellulose, nitroglycerin, RDX, and HMX used in a variety of propellant formulations. These will not be discussed in detail in this book, but there are a number of excellent books in print covering the field of propellants from the viewpoint of the chemist and the engineer (Kubota 2004).

The goal with a propellant is to maximize the volume, and temperature, of the hot gases produced from each gram of composition. Propellant theory predicts that the maximum thrust that can be obtained from a propellant is a function of the flame temperature and the average molecular weight of the exhaust gases produced when the propellant burns (Kubota 2004). Propellants generate a large volume of gas upon ignition and they thereby tend to show a significant increase in burn rate when confined. This is represented by the equation

$$\text{Burn rate} = aP^n \tag{9.1}$$

Where "a" is a constant determined by the propellant chemistry as well as manufacturing and testing variables, "P" is the pressure in the reaction chamber, and "n" indicates the exponential effect of a change in confinement pressure on burn rate. The value of "n" can be determined experimentally by burning compositions at different pressures (P) and measuring the burn rate. In general, the gassier the propellant, the higher the n value will be. Some representative values for propellant formulations are given in Table 9.1.

Propellants can generally be thought of as controlled-deflagration actions, which is readily apparent when considering projectiles such as rifle bullets where the propellant all burns in what appears to be an instantaneous fashion to the observer. However, rocket propellants, such as for model rockets or military missiles, are also deflagration actions even though all of the material is not consumed instantaneously to the human eye; the heat of the burning material propagates the reaction rapidly through the unreacted material, with hot gas venting in the opposite direction to generate thrust. If the burn was too slow, thrust would be insufficient, while if the burn was too fast and pressure built up too rapidly, a deflagration-to-detonation transition might occur, creating a shockwave and ultimately a detonation blast.

Propellants can be classified into two categories: homogenous, where a single molecule provides both fuel and oxidizer, and heterogeneous, which a mixture of

TABLE 9.1
Propellant Burn Rate Coefficients and Pressure Exponents[a]

Material		Pressure Exponent (n)
I.	Black powder	0.165
II.	Ammonium perchlorate PBAN, Al Composite	0.39
III.	Ammonium nitrate HTPB Mg	0.51
IV.	M10 single base Smokeless propellant	0.70
V.	M8 double base Smokeless propellant	0.83

PBAN, polybutadiene/acrylonitrile fuel/binder; TPB, hydroxy-terminated polybutadiene; "Smokeless propellant", nitrocellulose plus other additives; M8 double base, nitrocellulose (52%), nitroglycerine (43%), plus 5% other additives.

[a] Cooper (1996).

fuel and oxidizer like a traditional pyrotechnic mixture. Black powder, the first pyrotechnic, first explosive, *and* first propellant, is therefore a heterogeneous propellant (fuels: charcoal and sulfur, oxidizer: potassium nitrate).

THE ORIGINAL PROPELLANT: BLACK POWDER

Black powder remained the sole propellant available for military and civilian applications until well into the 19th century, and the production of the material flourished around the world. However, a number of problems associated with the manufacturing and use of black powder stimulated efforts to locate replacements. The issues included the following:

1. Substantial variation in burning behavior from batch to batch. The better black powder factories produced good powder if they paid close attention to the purity of their starting materials, used one source of charcoal, and did not vary the extent of mixing or the amount of residual moisture in their product.
2. Black powder has a relatively low gas output, on a per gram basis. Only about 50% of the products are gaseous; the remainders are solids.
3. The solid residue from black powder is highly alkaline (strongly basic), and it is quite corrosive to many materials.
4. Black powder is a fairly low-energy composition, with a heat combustion of approximately 0.66 kcal/g. In order to manufacture a "quick" energetic

> material from a composition with an energy output value this low, it is necessary to optimize the homogeneity of the material during the manufacturing process by a lengthy grinding operation involving a damp "cake" of powder. The consequence of this energetic mixing and grinding has been a cause for large number of accidents and explosions at black powder manufacturing sites. A 60:40 potassium perchlorate/aluminum "flash powder", in contrast, will produce about 2.4 kcal/g of heat output and therefore requires minimal mixing to yield a fast, energetic composition. Flash powders have low gas output, though, thereby precluding the use of these materials as propellants.

Replacement efforts had then been aimed at finding replacements for black powder that can give both enhanced performance as well as enhanced manufacturing safety. "Pyrodex®", the oldest and probably the best-selling of the replacement materials, is a patented pyrotechnic composition designed to fulfill many of the functions of black powder. It contains some of the ingredients found in black powder plus additional binders and burning rate modifiers that make the material somewhat less sensitive and slower burning at ambient pressure. A greater degree of confinement is required to obtain performance comparable to "normal" black powder though those are of course found inside barrels of firearms (Barrett 1984).

The advantages of black powder, and Pyrodex®, include good ignitibility, moderate cost, ready availability of the ingredients, and a wide range of uses (fuse powder, delay mixture, propellant, and explosive) depending on the degree of confinement.

However, as the use of black powder and Pyrodex® was understood and the advantages and disadvantages were well understood, the ideal features of a better propellant material became evident:

1. A propellant that can be prepared safely from readily available materials at moderate cost.
2. A material that readily ignites, but yet is stable during storage.
3. A mixture that forms the maximum quantity of low molecular weight gases upon burning, with minimum smoke or solid residue.
4. A mixture that burns at the highest possible temperature to provide maximum thrust.

SMOKELESS POWDERS

The late 19th century saw the development of a new family of "smokeless" powders, as modern organic chemistry blossomed and the nitration reaction (formation of a nitrate "ester" between the hydroxyl group of an alcohol and nitric acid) became commercially feasible to chemists around the world. Two nitrate esters—nitrocellulose (NC) and nitroglycerin (NG)—became the major components of these new propellants (as well as components in new explosive formulations). Figure 9.1 illustrates the formation of NC and NG from nitric acid and the precursor alcohols cellulose and glycerin.

Nitrocellulose consists of a chain of glucose molecules linked together to form a polymer chain. There are three hydroxyl (-OH) groups per glucose unit that are

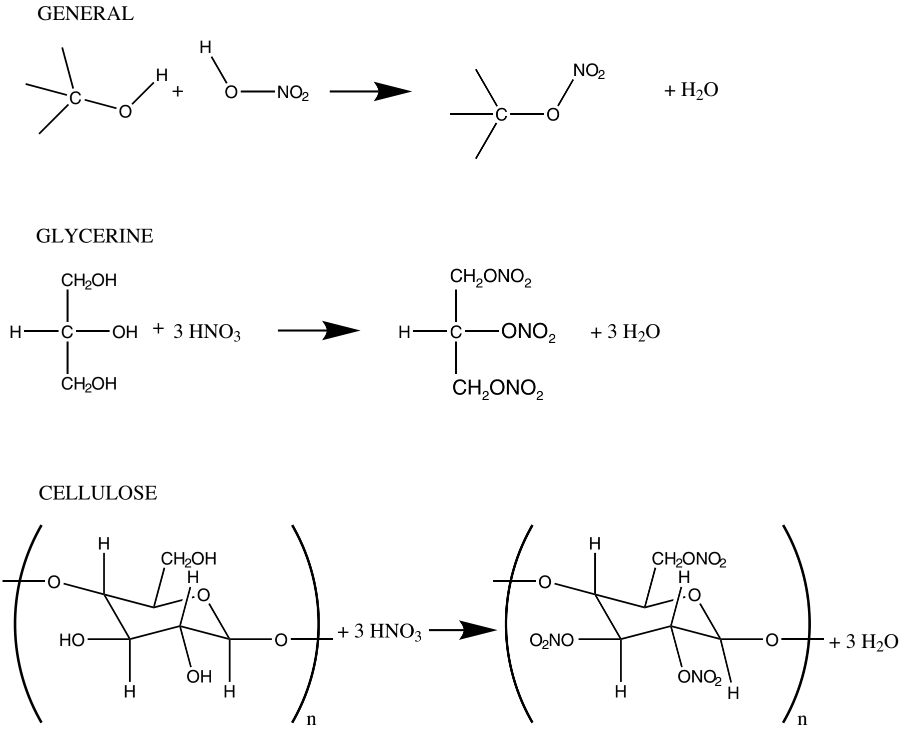


FIGURE 9.1 The nitration reaction. Organic compounds containing the -OH (hydroxyl) functional group are termed "alcohols." These compounds react with nitric acid to produce a class of compounds known as "nitrate esters." Nitroglycerine and nitrocellulose are among the numerous explosive materials produced using this reaction.

available for nitration. Full nitration results in a nitrogen content in the NC of approximately 14% by weight; material with a nitrogen content of 12.6% or better is generally considered to be "energetic" material. The heat of explosion of nitrocellulose is approximately 0.97 kcal/g (50% higher than the 0.66 kcal/g value for black powder), and the combustion products are 100% gases (Department of the U.S. Army 1984). Approximately 0.84 L of gas is evolved per gram of solid nitrocellulose.

"Single base" smokeless powder contains only nitrocellulose as an energetic material. "Double base" smokeless powder is a blend of nitrocellulose and nitroglycerin—the solid nitrocellulose is gelatinized by the liquid nitroglycerin. It might at first seem specious that nitroglycerin, used to make the first "modern" blasting explosive—dynamite—could also be used safely to make propellants. Nitroglycerin requires the shock from a blasting cap (or detonator) to cause reliable detonation of the material as an explosive. However, when it is blended with less-explosive materials and ignited with flame rather than shock, it is capable of more-routine burning (and not detonating) and was thus found to be quite useable and effective in propellant formulations. Recall the discussion that propellants work best when they are on the verge of, but not quite, exploding. Addition of nitroglycerin to nitrocellulose makes a more energetic burn to give greater thrust.

The heat of explosion for nitroglycerin is 1.5 kcal/g, and again the combustion products are all gases (approximately 0.72 L of gas per gram of nitroglycerin). The "double base" powders are the most energetic of the smokeless powders because of their nitroglycerin content, and the propellant energy increases as the nitroglycerin content is increased. Some double base powders have a nitroglycerin content of greater than 40%, and some of the double base powders are blasting cap-sensitive and classed as 1.1 explosives (Military Pyrotechnic Series Part One, "Theory and Application" 1967).

"Triple base" smokeless powder, containing nitroguanidine as a third component (up to 50% by weight), along with nitroglycerin and nitrocellulose, is also manufactured. This triple-base smokeless powder is the coolest burning of the three types of smokeless powder (nitroguanidine will reduce the flame temperature) and was developed for use in, and to extend the lifetime of, large and expensive metal gun barrels. The heat of explosion for nitroguanidine is 0.89 kcal/g—lower than either nitrocellulose or nitroglycerin. However, nitroguanidine releases approximately 0.89 L of gas per gram of material upon combustion, slightly better than either nitrocellulose or nitroglycerine. In effect, nitroguanidine will reduce flame temperature but also generate more gas. Triple-base smokeless powder will typically have reduced performance versus double-base though in many cases the advantage of extending the life of the projectile/gun barrel is worth the loss of overall efficacy. If reduced lifetime of the gun barrel is not important, but peak propellant performance is (such as with armor-piercing munitions), the nitroguanidine can be replaced with the military explosive RDX to substantially increase the performance and therefore projectile velocity.

All of the smokeless powders also contain an assortment of stabilizers, processing aids, flash inhibitors, and burn rate catalysts (Kubota 2004) (Department of the U.S. Army 1984).

An advantage of the smokeless powders is their ability to be *extruded* during the manufacturing process. Perforated grains can be produced that simultaneously burn inwardly and outwardly such that variable burning surface area and variable gas production versus time are achieved (Kubota 2004).

Nitrocellulose does not contain sufficient internal oxygen for complete combustion to CO_2, H_2O, and N_2, while nitroglycerin contains excess oxygen. The double base smokeless propellants therefore achieve a slightly more complete combustion and benefit from the substantial exothermicity of NG (approx. 1.5 cal/g) (Department of the U.S. Army 1984).

The smokeless powders were found to be much safer to manufacture than black powder, were more energetic per gram than black powder, produced essentially 100% gas products with a minimum of smoke[1] (and no corrosive solid products) when ignited. They burned much slower than black powder at standard atmospheric pressure, a safety feature in manufacturing. Under confinement, due to their large amount of gas products, they increased sharply in burn rate and were found to be noticeably faster—and performed better—than black powder at the typical high pressures found in gun barrels.

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[1] Smokeless powders are not truly "smokeless" and will produce some smoke and ash but far less than black powder and often not in any observable amount, thus giving rise to their name.

The only real downside to the nitrocellulose-containing powders was their inherent chemical instability. Traces of residual acid from the manufacturing process were difficult to completely remove from cellulosic materials, and this acid catalyzed the decomposition of the nitrate ester linkages in the nitrocellulose during storage. Small amounts of smokeless powder lost their ballistic performance over time as a result. Large amounts of smokeless powder stored in sealed containers could undergo accelerating self-heating, since both the heat that was generated and the additional acid catalyst generated during the decomposition of the nitrate ester linkages caused rate acceleration in the center of large containers. If the temperature inside a drum of smokeless powder reached the low (approximately 200°C) ignition temperature of the material, ignition—leading to an explosion—could result, and a warehouse would disappear (recall the time-to-explosion study in Figure 6.7).

This problem was eventually solved—in a classic example of applied acid/base chemistry—by the incorporation (at a 1%–2% level) of a small percentage of an "antiacid" into the smokeless propellant composition. The material used for over a century to stabilize single base smokeless powder is diphenylamine, $C_{12}H_{11}N$—a solid derivative of ammonia, with two 6-carbon benzene rings replacing hydrogen atoms on the ammonia molecule, as shown in Figure 9.2. The basic nitrogen in the diphenylamine molecule picks up any acidic hydrogen ions, H^+, that are produced upon decomposition of the nitrocellulose, and the 6-carbon benzene rings are effective absorbers of nitrogen oxides, also generated during the decomposition of nitrocellulose. The removal of these chemical species by the diphenylamine stabilizer blocks any acceleration of the rate of decomposition of the nitrocellulose, extending the lifetime of the smokeless powder for many years. Similar chemical stabilizers are added to double base and triple base smokeless powders as well. Diphenylamine is not normally used with these materials (it is too basic to be compatible in storage with nitroglycerin), and weaker organic bases are used instead.

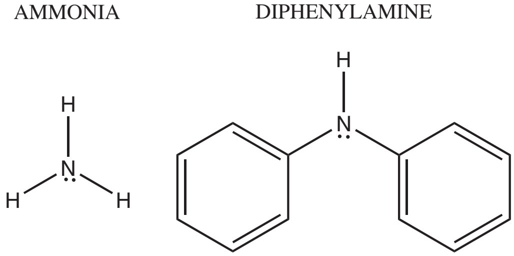

FIGURE 9.2 Molecular structures for ammonia (a gas at ambient conditions), and its nitrocellulose-storage stabilizing derivative diphenylamine (a solid at ambient conditions). The basic nitrogen acts as a base for hydrogen ions, and the benzene rings will absorb nitrogen oxides. Diphenylamine saved the nascent smokeless powder industry, and still helps it today, by making nitrocellulose safer in storage.

Smokeless powders are widely used today as the propellants for small arms ammunition as well as for artillery projectiles. Black powder use fell dramatically as the 20th century began, with the introduction of the smokeless propellants, but it remains the primary propellant used by the fireworks industry for sky rockets and for aerial shells fired from mortars and is still used for a variety of military applications as well.

(Sometimes the opposite of smokeless powders is desired: the generation of as much smoke, solid products dispersed in the air, as possible. This will be discussed in Chapter 11)

PROPELLANTS FOR LAUNCH VEHICLES

The larger rockets and missiles used by the military and in the space program require *tremendous* thrust to overcome gravity in both lifting off and attaining high altitudes successfully, so combinations of liquid fuel "engines" with solid propellant "pyrotechnic" boosters are used to lift enormous vehicles, such as the launch rockets for the legacy NASA Space Shuttle and eventually the Space Launch System (SLS) heavy launch vehicle. These liquid fuel engines can include hydrogen peroxide (H_2O_2) and hydrazine (N_2H_4), or liquid hydrogen (H_2) with liquid oxygen (O_2).

Modern solid propellants for rocket and missile technology have relied for quite a few decades now on "composite propellants" that appear "pyrotechnic" in their makeup. They are usually based on ammonium perchlorate (NH_4ClO_4) as the oxidizer. Various polybutadiene (synthetic rubber) derivatives are commonly used as the primary fuel and also play a role as a binder for the compositions. Ammonium perchlorate produces 100% gas products during its thermal decomposition and therefore is an excellent choice for use in solid propellants. The pyrotechnic boosters used for these launches typically contain the following:

1. *A solid oxidizer*: Ammonium perchlorate (NH_4ClO_4, or "AP") is the current favorite due to the high percentage of gaseous products it forms upon reaction with a fuel.
2. *An organic fuel that also serves as binder and gas-former*: Liquids that polymerize into solid masses are preferred, for simpler processing, and a binder with low oxygen content is desirable to maximize heat production per pound.
3. *A small percentage of light, high-energy metal*: This metal produces solid combustion products that do not aid in achieving thrust, but the considerable heat evolved by the burning of the metal raises the temperature of the other gaseous products, producing greater thrust. Another very significant role played by the metal fuel is that of a thermal conductor, capturing some of the heat produced as the propellant burns and effectively conducting this heat into the column of unburned propellant. The thermal conductivity of the metal helps smooth out the burning of the propellant as well. Aluminum and magnesium are the metals that have been most commonly used.

The formulation for the Space Shuttle booster rockets is as follows (NASA—Solid Rocket Boosters 2006):

Ammonium perchlorate	70
Polybutadiene polymer[a]	12
Aluminum	16
Epoxy	2
Iron oxide	0.17

[a] A polybutadiene-acrylic acid-acrylonitrile terpolymer, also referred to as polybutadiene acrylonitrile "PBAN".

The iron oxide serves as a burn rate catalyst, speeding up the thermal decomposition of the ammonium perchlorate. Other metal oxides have been shown to also display catalytic effects with ammonium perchlorate, such as cupric oxide, CuO, and cobalt oxide, Co_2O_3. Little use of catalysts is otherwise seen with pyrotechnic-type compositions, where the goal is to control, rather than maximize, burn rate.

Each booster on the legacy Space Shuttle contained ~1 million pounds of solid propellant, meaning a total of 2 million pounds of propellant functions each time the Space Shuttle was launched (Seltzer 1998). A negative oxygen balance (i.e., a fuel-rich composition with positive net Pyro Valence) is frequently designed into these propellant mixtures to obtain CO gas in addition to CO_2. CO is lighter and will produce greater thrust, all other things being equal. However, the full oxidation of carbon atoms to CO_2 evolves more heat, so some trial-and-error is needed to find the optimum ratio of oxidizer and fuel.

PROJECTILE VS. ROCKET PROPELLANTS

As we have seen, the type of materials used in projectile (gun) propellants and those used for large rocket propellants are different. Gun propellants tend to be homogenous (nitrocellulose), while rocket propellants tend to be heterogeneous (ammonium perchlorate oxidizer, polybutadiene and aluminum fuels). In projectile/gun-type systems, the propellant rapidly burns at an extremely high pressure to instantaneously move the intended projectile/bullet (with single fast pulse of pressure/thrust). Rockets, in contrast, require a sustained burning over a longer period of time to give continuous thrust through the course of the rocket's path. J. Akhavan reports that rocket propellants will burn with a chamber pressure of ~7 MPa (~69 atm), while gun-type propellants will approach 400 MPa (nearly 4,000 atm!) (Akhavan 2004).

To create this kind of sustained burning for rocket propellants, the *heterogeneous* material is often loaded into the engine in granulated form to burn more uniformly. For gun/projectile type systems where a complete burn is required immediately to create the required pressures, the *homogenous* propellant is pressed into a single quantity to burn, if not instantaneously, very rapidly and linearly, like a fuse.

MODERN APPROACHES IN PROPELLANTS

More recent propellant research has focused on the use of the chemically similar nitramine explosives RDX (Research Department Explosive) and HMX (High Melting Explosive or Her Majesty's Explosive) as energetic materials. Structures for RDX and HMX are shown in Figure 9.3.

Like nitrocellulose, these materials will ignite and burn in a controlled manner from a flame stimulus and yet detonate when a shock of sufficient energy is applied. RDX ($C_3H_6N_6O_6$, Pyro Valence to CO_2=+6) and its chemical first-cousin HMX ($C_4H_8N_8O_8$, Pyro Valence to CO_2=+8) are both slightly fuel-rich to produce carbon dioxide as a reaction product but are *oxygen-balanced* (Pyro Valence=0) to form water, nitrogen, and carbon monoxide, CO, as combustion products. These "high explosives" are blended with a binder and, in some cases, ammonium perchlorate, to produce propellant formulations. The binders in these propellants are selected to also serve to desensitize these propellants to impact and shock, and make them safer to handle, transport, and store.

Propellant compositions have also been used in automobile air bags (originally highly volatile sodium azide, NaN_3), as well as in numerous other "gas generator" devices, where the production of gas pressure is used to drive pistons, trigger switches, eject pilots from aircraft, and perform an assortment of other critical functions. The military and the aerospace industry use many of these items, which can be designed to function rapidly and can be initiated remotely.

Research continues in efforts to produce propellant materials that meet all of the requirements of the 21st century—superior performance, safety in manufacturing and storage, and environmental compatibility. For example, ammonium nitrate has been investigated as an alternative for ammonium perchlorate, and certain binding polymers have been nitrated to make them additionally energetic, such as polyvinyl nitrate.

Furthermore, physical engineering of propellant "engine" geometries has been also a major focus of research. Solid propellants in an engine can be "core burning," "end burning," or one several other types of geometrically actuated burning

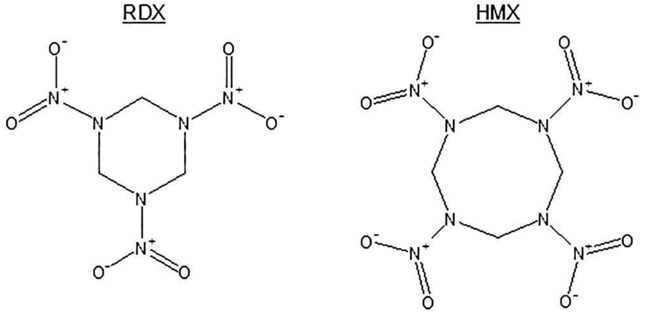

FIGURE 9.3 Molecular structures for RDX and HMX. These high-explosives will detonate if subjected to a blasting cap or other suitable shock stimulus but have also found utility as propellants when combusted in mixtures with binders and occasionally oxidizers.

techniques to meet the need of the device. Propellant formulations can also be granulated into grains, extruded into single solid masses, and loaded into the container in a homogenous manner (same chemical mix throughout) or a heterogeneous manner (differing physical or chemical makeup).

Propellant chemists and engineers have a variety of tools and options at their disposal in the far-reaching propellant subclass of energetic materials.

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10 Light and Color Production

A FUSEE: The highway flare, or "fusee", is an intriguing pyrotechnic article, requiring a long burn time and good candlepower from the red flame. An item with long burn time is relatively easy to make. An item with high candlepower is relatively easy to make. An item with both long burn time and high candlepower is indeed a challenge, requiring just the right chemistry and technology in the manufacturing process.

> No one appreciates a firework display as much as a chemist does. When a beautiful red and blue chrysanthemum shell explodes up in the sky, 99% of the audience goes "ooooh," while the chemist knows "aah, strontium and copper..."

INTRODUCTION

The production of bright light, often with vivid color, is the primary purpose of many pyrotechnic compositions. Light emission has a variety of applications, ranging from military signals and illuminating devices to highway distress flares to spectacular aerial fireworks shows and theatrical pyrotechnics. The basic theory of light emission was discussed in Chapter 2, and several good articles have been published dealing with the chemistry and physics of colored flames (Douda, *Theory of Colored Flame Production* 1964) (Kosanke and Kosanke 2004).

Color compositions can be pressed into tubes to produce flares of varying burn times, or the compositions can be pressed into pellets and fired or expelled into the air. The aerial pellets are referred to as "stars," and a large star fired singly is often referred to as a "comet." Very small stars are also now widely used in fireworks fountains, where an expelling charge of a black powder-type composition sprays small "microstars" into the air to produce spark-type effects of various colors (T. Shimizu, Studies in microstars 1985).

The instrumentation used for the analysis of the light emission from pyrotechnic mixtures has continued to get better and better, providing scientists with more and more information regarding the molecular and atomic origin of light emission. However, the quantitative measurement of "light intensity" (candlepower) at any single moment as well as the "light integral" (total energy emitted, with units of candle-seconds/gram) can be affected by a variety of test parameters such as container diameter, burning rate, and even uncertainty in the measuring equipment. Therefore, comparisons between data obtained from different reports—using either different equipment of a different test procedure—should be viewed with an understanding of the variability and uncertainty.

WHITE-LIGHT COMPOSITIONS

Overview of White-Light Production

For white-light emission, a mixture is required to burn at high temperature (typically greater than 3,000°C), creating a substantial quantity of excited atoms or molecules in the vapor state together with incandescent solid or liquid particles.[1] Incandescing particles will emit a broad range of wavelengths in the visible region of the electromagnetic spectrum, and which is then perceived by the human eye as white (or near-white) light. Intense emission from sodium atoms in the vapor state, excited to higher energy electronic states by high flame temperature, is the principal light source in the sodium nitrate–magnesium–organic binder flare compositions widely used by the military (Douda, *Spectral Observations in Illuminating Flames* 1968) (Dillehay 2004). While sodium emits in a spectral range that the human eye perceives as yellowish light (see below), the heat of the system will produce an intense enough emission that comes off as white.

Magnesium or aluminum are found as fuels in most white-light compositions. These metals evolve substantial heat upon oxidation, and the high-melting magnesium oxide (MgO) and aluminum oxide (Al_2O_3) reaction products are good light emitters at the high reaction temperatures that can be achieved using these fuels. Titanium and zirconium metals are also good fuels for white-light compositions, but their spark sensitivities require caution in manufacturing if fine fuel particles are used.

In selecting an oxidizer and fuel for a white-light mixture, a main consideration is maximizing heat output. A value of 1.5 kcal/g has been given by Shidlovskiy as the minimum for a usable illuminating composition (Shidlovskiy 1964). Black powder produces a heat output of approximately 0.66 kcal/g, whereas sodium nitrate/magnesium and potassium perchlorate/aluminum compositions produce a heat output in excess of 2 kcal/g and are noticeably brighter and whiter in their flame color.

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[1] Recall that "incandescence" is the emission of visible light from a hot material, such as a classic hot-wire light bulb or molten metal.

A flame temperature of less than 2,000°C will produce a minimum amount of white light by emission from incandescent particles or from excited gaseous sodium atoms. Therefore, the initial choice for an oxidizer is one with an *exothermic* heat of decomposition such as potassium chlorate ($KClO_3$). However, binary mixtures containing either a chlorate or perchlorate salt with active metal fuels are usually considered *too* ignition-sensitive for commercial use, and the less-reactive, but safer, nitrate compounds are usually selected. Potassium perchlorate is used with aluminum and magnesium in some "photoflash" mixtures (see below), which are extremely reactive compositions, with velocities in the explosive range and intense white-light output. Care in manufacturing and small quantities in process at any given time is usually employed—and strongly recommended—with these mixtures.

While nitrates are considerably endothermic in their decomposition and therefore deliver less heat per mole than chlorates or perchlorates, they can be used with somewhat less fear of accidental ignition and therefore have a better safety profile. However, if fine metal fuel particles are used, static electricity is always a concern regardless of the oxidizer that is used.

Barium nitrate—$Ba(NO_3)_2$—has often been selected for use in white-light mixtures. The barium oxide (BaO) product formed upon reaction is a good, broad-range molecular emitter in the vapor phase (the boiling point of BaO is ca. 2,000°C), and condensed particles of BaO found in the cooler parts of the flame are also good emitters of incandescent light. However, the toxicity of barium should be a consideration in oxidizer selection depending on the totality of the circumstances.

Sodium nitrate—$NaNO_3$—is another frequent choice for white-light production. It is quite hygroscopic, however, so precautions must be taken during production and storage to exclude moisture. Sodium nitrate produces good heat output per gram due to the low atomic weight (23) of sodium, and the intense flame emission from atomic sodium in the vapor state contributes substantially to the total light intensity. Potassium nitrate—KNO_3—on the other hand, is *not* a good source of intense atomic or molecular emission, and it is rarely (if ever) used as the sole oxidizer in white-light compositions, even though potassium is just below sodium on the Periodic Table of Elements and they share many other characteristics.

ILLUMINATING COMPOSITIONS AND FLARES

Illuminating compositions, or "illuminants," and flares ideally produce bright light for a long duration of time, both for lighting an area (illuminants) and for signaling purposes (flares).

Magnesium metal is the fuel found in most military illuminating compositions, as well as in some "special effects" devices. However, it is rarely used in fireworks, due to moisture concerns. Aluminum and titanium metals, the magnesium/aluminum alloy "magnalium," and antimony trisulfide (Sb_2S_3) are used for white-light effects in many fireworks mixtures. Several published formulas for white-light compositions are given in Table 10.1.

TABLE 10.1
White Light Compositions

Oxidizer (% by Weight)			Fuel (% by Weight)		Other (% by Weight)		Reference
I.	Barium nitrate, $Ba(NO_3)_2$	38.3	Magnesium, Mg	26.9	Wax	6.7	Shimizu, T. in R. Lancaster (1972)
	Potassium nitrate, KNO_3	25.2			Oil	2.9	
II.	Sodium nitrate, $NaNO_3$	44	Magnesium, Mg	50	Laminac	6	Winokur (1978)
III.	Teflon, $(\text{-}CF_2\text{-}CF_2\text{-})_n$	46	Magnesium, Mg	54	Nitrocellulose	2.6	Winokur (1978)
IV.	Sodium nitrate, $NaNO_3$	53	Aluminum, Al	35	"VAAR" resin	5	Winokur (1978)
			Tungsten, W	7			
V.	Potassium perchlorate, $KClO_4$	64	Antimony, Sb	13	Gum	10	Shidlovskiy (1964)
	Potassium nitrate, KNO_3	13					
VI.	Potassium nitrate, KNO_3	65	Sulfur, S	20	Fine black powder	5	Shidlovskiy (1964)
			Antimony, Sb	10			
VII.	Ammonium perchlorate, NH_4ClO_4	40	Antimony sulfide, Sb_2S_3	14	Wood meal	5	Shidlovskiy (1964)
	Potassium perchlorate, $KClO_4$	30	Starch	11			

Extremely bright compositions can be produced using an oxidizer with zirconium as the fuel. The high boiling point of zirconium oxide, well in excess of 4,000°C, allows the flame temperature to rise to extraordinary levels approaching 5,000°C, producing a brilliant white light. This effect has seen little commercial application, however, due to the extreme spark-sensitivity associated with compositions containing zirconium powders.

The ratio of ingredients, as expected, will affect the performance of the composition. Optimum performance is anticipated near the stoichiometric point, but an excess of metallic fuel usually increases the burning rate and light emission intensity. The additional metal increases the thermal conductivity of the mixture, thereby increasing the burn rate, and the excess fuel, especially a volatile metal such as magnesium (boiling point 1,107°C), can vaporize and burn with oxygen in the surrounding air to produce extra heat and light.

The sodium nitrate/magnesium system is extensively used for military illuminating compositions. Data for this system are given in Table 10.2. The anticipated reaction between sodium nitrate and magnesium is

$$5Mg + 2NaNO_3 \rightarrow 5MgO + Na_2O + N_2 \tag{10.1}$$

For a stoichiometric mixture, 121.5 g of magnesium and 170 g of sodium nitrate correspond to the balanced chemical equation (41.6% magnesium and 58.4% sodium nitrate by weight). Formula A in Table 10.2 therefore contains an excess of oxidizer. It is the slowest burning mixture and produces the least heat. Formula B is very close to the stoichiometric point. Formula C contains excess magnesium and is the most reactive of the three; the burning of the excess magnesium in the air appears to contribute substantially to the performance of this composition.

A common military flare composition is MTV, or magnesium–Teflon–Viton, with magnesium as the metal fuel, Teflon (polytetrafluoroethylene) as the main oxidizer, and Viton as a secondary oxidizer and binder. This flare emits strongly in both the visible region as well as in the infrared and found usefulness as a "decoy" for heat-seeking missiles (see further discussion at the end of this chapter).

A significant altitude effect will be shown by these illuminating compositions, especially those containing excess metal. The decreased atmospheric pressure, and also the resulting decrease in oxygen concentration, at higher altitudes will slow the burning rate as the excess fuel will not be consumed as efficiently by the lower concentrations of atmospheric oxygen, and the reduced atmospheric pressure will not hold the heat at the reaction surface as effectively as a higher pressure does.

Illuminant compositions are typically mixtures of an oxidizer, metal fuel, and binder. They provide a classic example of how to modify the performance of a pyrotechnic

TABLE 10.2
The Sodium Nitrate/Magnesium System (Shidlovskiy 1964)

	% Sodium Nitrate	% Magnesium	Linear Burning Rate (mm/s)	Heat of Reaction (kcal/g)
A.	70	30	4.7	1.3
B.	60	40	11.0	2.0
C.	50	50	14.3	2.6

mixture. For a faster (and brighter) reaction, several options are available—use a higher percentage of the metal fuel, use a finer particle size metal, or reduce the binder content to raise the heat output. Criteria such as cost, performance, and specification limitations will determine which approach is best for a given situation.

"PHOTOFLASH" MIXTURES

A photoflash composition – sometimes just called "flash powder" – is one that produces an intense burst of light for an extremely short duration, typically a fraction of a second. To generate this effect, a composition is required to react very rapidly in addition to having a hot flame temperature. Fine particle sizes are used for the oxidizer and the (often metallic) fuel to increase reactivity, noting of course that sensitivity is also enhanced as the same time. Therefore, these photoflash mixtures are quite hazardous to prepare, and mixing operations should always be carried out remotely. Several representative photoflash mixtures are given in Table 10.3. Note that "hot" metal fuels are used in all examples, along with the equally potent potassium perchlorate in several. Barium nitrate, noting its white-light emitting characteristics discussed previously, is also included.

An innovation in military photoflash technology was the development of devices containing fine metal powders *without* any oxidizer. A high-explosive bursting charge is used instead. This charge, upon ignition, scatters the metal particles at high temperature, and they are then air-oxidized to produce light emission also known as a "thermobaric" system (from the Greek words for "heat" and "pressure"). No

TABLE 10.3
Photoflash Mixtures

	Oxidizer (% by Weight)		Fuel (% by Weight)		Reference
I.	Potassium perchlorate, $KClO_4$	40	Magnesium, Mg	34	Shimizu, T. in R. Lancaster (1972)
			Aluminum, Al	26	
II.	Potassium perchlorate, $KClO_4$	40	Magnalium, Mg/Al	60	Shimizu, T. in R. Lancaster (1972)
III.	Potassium perchlorate, $KClO_4$	30	Aluminum, Al	40	Shimizu, T. in R. Lancaster (1972)
	Barium nitrate, $Ba(NO_3)_2$	30			
IV.	Barium nitrate, $Ba(NO_3)_2$	54.5	Magnalium	45.5	Winokur (1978)
			Aluminum	4	
V.	Sodium periodate	40	Magnalium	60	Brusnahan, et al. (2017) "Green pyrotechnics" barium/perchlorate-free binary flash

hazardous mixing of oxidizer and fuel is required to prepare these illuminating devices though fine metal particles may still be sensitive to static electricity discharge.

Energetic photoflash compositions require a minimum of mixing in order to create highly reactive oxidizer–fuel blends. It is possible to mix these compositions in the actual end item by placing layers of oxidizer and fuel in the device, sealing the units, and then gently tumbling or rotating the devices, in a remote location, to achieve an acceptable degree of homogeneity for the powder inside the device. Similarly, flash powders used in the entertainment industry as special effect materials are shipped and stored as separate, premeasured containers of oxidizer and fuel. Right before "show time," the chemicals are carefully blended, loaded into holders, positioned for use, and then electrically fired at the proper moment during a show—producing a concussive audible effect and a flash of light.

Flash powders are among the most energetic, sensitive, and explosive of all binary pyrotechnic compositions. There is sometimes debate and friendly discussion about whether or not very reactive flash powders function by a deflagration (extremely rapid burning) or a detonation (supersonic reaction front) mechanism. It is truly an academic argument: There is no question that they can *violently* explode, whatever the reaction process is.

"Green Pyrotechnics" for Photoflash Compositions

As apparent in Table 10.3, classic photoflash compositions all use the highly potent potassium perchlorate or barium nitrate as oxidizers for the compositions. As discussed, barium and perchlorates both pose toxic problems that warrant replacement. One recent advancement has been in the use of periodates, IO_4^-, instead of perchlorates, specifically sodium periodate, $NaIO_4$, to use both the "green" oxidizing potential of the periodate as well as the spectral emission of the sodium atom to achieve the required illumination "photoflash" effect. Research by Brusnahan shows a 60% magnalium and 40% sodium periodate mixture ignites with a strong luminous intensity and may be a replacement for perchlorate compositions (Brusnahan, et al. 2017). Further research by Moretti showed that this composition burned slightly faster than a barium nitrate/potassium perchlorate/magnalium control, with an even better luminous efficiency (Moretti, et al. 2012).

SPARK PRODUCTION

The production of brilliant sparks—tiny incandescent particles discharged from a main system—is one of the principal effects available to the fireworks manufacturer and to the "special effects" industry. Sparks occur during the burning of many pyrotechnic compositions, and they may or may not be a desired feature.

Sparks are produced when liquid or solid particles, either original components or reaction products created at the burning surface, are ejected from the composition by gas pressure produced during the high-energy reaction. These particles, heated to incandescing temperatures, leave the flame area and proceed to radiate light as they cool off or continue to react with atmospheric oxygen traveling through open atmosphere. The particle size of the fuel will largely determine the quantity and size of sparks: the larger the particle size, the larger the sparks are likely to be. A combination consisting of fine fuel particles for heat production blended with larger fuel particles for the spark effect is a technique that has been used by some manufacturers (and is what is found in many common handheld consumer "sparklers").

Metal particles, especially aluminum, titanium, and "magnalium" alloy, produce good sparks that are white in appearance. Charcoal of sufficiently large particle size also works well, producing sparks with a characteristic orange color (often seen in ground-fountain fireworks). Sparks from iron particles vary from gold to white, depending on the reaction temperature; they are the source of many of the brilliant sparks seen in the popular handheld "gold sparkler" ignited by millions of people on the 4th of July.

Magnesium metal, however, does not produce a good spark effect unless a substantially large particle size metal is used. The metal has a low boiling point (1,107°C) and therefore tends to vaporize and completely react in the pyrotechnic flame (Shimizu, T. in R. Lancaster 1972). "Magnalium" can produce good sparks that burn in air with a novel, crackling sound.

Several spark-producing formulas are given in Table 10.4. Remember, the particle size of the spark-producing material is very important in generating sparks in a

TABLE 10.4
Spark-Producing Compositions

Composition		% by Weight	Effect	Reference
I.	Potassium nitrate, KNO_3	58	Gold sparks	Shidlovskiy (1964)
	Sulfur	7		
	Pure charcoal	35		
II.	Barium nitrate, $Ba(NO_3)_2$	50	Gold sparks (sparkler)	Shidlovskiy (1964)
	Steel filings	30		
	Dextrine	10		
	Aluminum powder	8		
	Fine charcoal	0.5		
	Boric acid	1.5		
III.	Potassium perchlorate, $KClO_4$	42.1	White sparks	Jennings-White, Chapter 14: Glitter Chemistry (2004)
	Titanium	42.1		
	Dextrine (make a paste from dextrine and water, then mix in oxidizer and fuel)	15.8		
IV.	Potassium perchlorate, $KClO_4$	50	White sparks "waterfalls"	Shidlovskiy (1964)
	"Bright" Al powder	25		
	"Flitter" Al, 30–80 mesh	12.5		
	"Flitter" Al, 5–30 mesh	12.5		

pyrotechnic flame; experimentation is needed to find the ideal size for a given effect. For a good spark effect, the fuel must contain particles large enough to escape from the flame prior to complete combustion. Also, the oxidizer must not be too effective, or complete reaction may occur in the flame, and little or no spark effect will be observed. Charcoal sparks are difficult to achieve with the hotter oxidizers; potassium nitrate (KNO_3), with its lower flame temperatures, often works best. Some gas production is required to achieve good spark effects by assisting in the ejection of particles from the flame. Charcoal, other organic fuels and binders, and the nitrate ion can provide gas for this purpose.

STROBES AND "TWINKLERS"

The ability of certain compositions to burn in a pulsing, light/dark oscillation "strobe light" manner is a novel phenomenon where the light intensity is very strong and then dark, cycling like this while the composition completes burning. Chemically, pyrotechnic strobes are believed to involve two distinct reactions, as originally noted by Shimizu. A slow, "dark" process occurs until sufficient heat is generated to initiate a fast, light-emitting reaction. Dark and light reactions continue in an alternate manner, generating the strobe effect (T. Shimizu, Studies on strobe light pyrotechnic compositions 1982) (Jennings-White, Chapter 15: Strobe chemistry 2004). This phenomenon has been investigated and some research results and discussion published even recently (Corbel, et al. 2013).

One possibility that is suspected to give rise to this effect is that the initial "light" reaction on the surface of a pressed strobe mixture creates a hard crust on top of the composition, with the "dark" smolder process still going on underneath. The dark process creates gaseous species that build pressure. The crust is eventually broken through, with light-emitting effect, when the heat and pressure below it is sufficient, eventually creating another surface crust, and so on. Another possibility considered is that the pyrotechnic reaction is happening at two distinct rates because of a thermal feedback loop or oxygen influx. It is often seen that the frequency of the strobe pulse will increase as the composition is burned, or in other words, less of a delay between bright flashes before completion.

Corbel et al. note that a common magnesium–ammonium perchlorate binary mixture undergoes the strobe effect and surmise that this composition undergoes a "two-stage" burning (Corbel, et al. 2013). First, the magnesium particles are vaporized in the heat of the reaction and oxidized by ambient air after being ejected above the surface, the "light" zone. The mixture then smolders through metal–oxidizer reaction, the "dark" zone, to generate enough heat to vaporize and eject the magnesium again to create the light effect, etc. With magnalium (a common strobe fuel), the magnalium is suspected to decompose into magnesium and aluminum, wherein the aluminum reacts with the oxidizer to generate heat and vaporize the magnesium for air oxidation, creating the "light" zone as previously mentioned. Addition of barium sulfate (a common strobe additive, among others) helps this effect by creating a solid layer on the surface and absorbing heat, delaying the evaporation of magnesium, enhancing the overall strobe effect.

Some strobe formulations, sometimes also called "twinklers," are given in Table 10.5. In general, the compositions include both a "light" and a "dark" reaction

TABLE 10.5
Strobe Compositions[a]

	Strobe Color (% by Weight)		
Material	**Red**	**Green**	**White**
Ammonium perchlorate	50	60	60
Strontium sulfate	20		
Barium Sulfate		17	15
Magnesium	30	23	
Magnalium alloy			25
Potassium dichromate	+5	+5	+5

Potassium dichromate is coated on the metal fuel as a stabilizer.

[a] T. Shimizu, Studies on Strobe Light Pyrotechnic Compositions (1982).

binary pyrotechnic. For example, the "white strobe" in Table 10.5 shows a combination of ammonium perchlorate, barium sulfate, and magnalium. Magnalium and barium sulfate is a known flash powder, for the "light" reaction, while magnalium and ammonium perchlorate is known to smolder, for the "dark" reaction. An in-depth investigation of this "light-and-dark reaction" hypothesis was undertaken by Jennings-White with discussion on 13 different strobe compositions (Jennings-White, Strobe Chemistry 2004). A further investigation was undertaken by Corbel et al. that recorded light intensity studies and high-speed cameras to record the effect (Corbel, et al. 2013).

The strobing light production from these compositions can be used for entertainment, but it also offers some interesting possibilities for emergency signaling flares.

OTHER LIGHT EFFECTS: FLITTER AND GLITTER

Several other interesting visual effects can be achieved by careful selection of the fuel and oxidizer for a spark-producing composition. Several thorough review articles discussing this topic in detail, with numerous formulas, have been published (Winokur 1978) (Jennings-White, Chapter 14: Glitter chemistry 2004).

"Flitter" refers to the large white sparks obtained from the burning of large aluminum flakes. These flakes burn continuously upon ejection from the flame, creating a beautiful white effect, and they are used in a variety of fireworks items.

"Glitter" is the term given to the effect produced by molten metal droplets which, upon ejection from the flame, ignite in air to produce a brilliant flash of light. A nitrate salt (KNO_3, again, is best) and sulfur or a sulfide compound appear to be essential for the glitter phenomenon to be achieved. It is likely that the low melting point (334°C) of potassium nitrate produces a liquid phase that is responsible, at least in part, for this effect. Several "glitter" formulas are given in Table 10.6.

TABLE 10.6
Glitter Formulas[a]

Composition		% by Weight	Effect	Note
I.	Potassium nitrate, KNO_3	55	Good white glitter	Used in aerial stars
	"Bright" Al powder	5		
	Dextrine	4		
	Antimony sulfide, Sb_2S_3	16		
	Sulfur	10		
	Charcoal	10		
II.	Potassium nitrate, KNO_3	55	Gold glitter	Used in aerial stars
	"Bright" Al powder	5		
	Dextrine	4		
	Antimony sulfide, Sb_2S_3	14		
	Charcoal	8		
	Sulfur	8		
III.	Potassium nitrate, KNO_3	55	Good white glitter	Used in fountains
	Sulfur	10		
	Charcoal	10		
	Atomized aluminum	10		
	Iron oxide, Fe_2O_3	5		
	Barium carbonate, $BaCO_3$	5		
	Barium nitrate, $Ba(NO_3)_2$	5		

[a] Winokur (1978).

COLORED-LIGHT PRODUCTION

OVERVIEW OF COLORED-LIGHT PRODUCTION

Certain elements and chemical compounds, when heated to high temperature, and are present in the pyrotechnic flame in the vapor phase, have the unique property of emitting lines or narrow bands of light in the visible region (380–780 nm) of the electromagnetic spectrum. This emission is perceived as color by an observer, and the production of colored light is one of the more important goals sought by the pyrotechnic chemist. Table 10.7 lists the colors associated with the various regions of the visible spectrum. The *complementary* colors, perceived if white light *minus* a particular portion of the visible spectrum is viewed, are also given in Table 10.7. The dyes used to produce colored smoke (see Chapter 11) have their observed color by this latter principle: absorbing a portion of visible light and scattering the remainder.

To produce color in a pyrotechnic flame, heat (from the reaction between an oxidizer and a fuel) and a color-emitting species are required. Sodium compounds added to a heat mixture will impart a yellow–orange color to the flame. Strontium salts and lithium will yield red, barium and certain boron or copper compounds can give green, and certain other copper-compounds will produce blue. Color can be

TABLE 10.7
The Visible Spectrum[a]

Wavelength (nm)	Emission Color	Complementary Color
<380	None (ultraviolet region)	–
380–435	Violet	Yellowish-green
435–480	Blue	Yellow
480–490	Greenish-blue	Orange
490–500	Bluish-green	Red
500–560	Green	Purple
560–580	Yellowish-green	Violet
580–595	Yellow	Blue
595–650	Orange	Greenish-blue
650–780	Red	Bluish-green
>780	None (infrared region)	–

Complementary colors are the observed colors if the emission color wavelength is *removed* from white light.

[a] Bauer, et al. (1979).

produced by emission of a narrow band of light (e.g., light in the range 435–480 nm is perceived as blue) or by the emission of several ranges of light that combine to yield a particular color. For example, the mixing of blue and red light in the proper proportions will produce a purple–violet flame effect, while mixing red and green light in the proper proportions will produce a yellow flame effect (recall these are *emissive* or *additive* colors and do not mix like paint). While all children learn their basic colors early in life, Color Theory is a complex topic, but it is one that should be studied by anyone desiring to produce colored flames (Kosanke and Kosanke 2004).

A catalog of emission colors from a selection of more common pyrotechnic products and their corresponding wavelengths in nanometers is shown in Table 10.8 (Meyerriecks and Kosanke 2003) (Sabatini 2018) (Douda, *Theory of Colored Flame Production* 1964).

The production of a vividly colored flame is a much more challenging problem than creating white light. A delicate balance of factors is required to obtain a satisfactory effect:

1. An atomic or molecular species that will emit the desired wavelength, or blend of wavelengths, must be present in the pyrotechnic flame.
2. The emitting species must be sufficiently volatile to exist in the vapor state at the temperature of the pyrotechnic reaction. The flame temperature will range from 1,000°C to 2,000°C (or more), depending on the particular composition used.
3. Sufficient heat must be generated by the oxidizer–fuel reaction to produce the excited electronic state of the emitter. A minimum heat requirement of 0.8 kcal/g has been mentioned by Shidlovskiy (Shidlovskiy 1964).
4. Heat is necessary to volatilize and excite the emitter, but you must not *exceed* the dissociation temperature of molecular species (or the ionization

TABLE 10.8
Colors Produced by Pyrotechnic Reaction Products and Corresponding Wavelengths[a–c]

Emission Color	Light-Emitting Species	Primary Wavelengths (Approximate, nm)
Red		600–700 (overall)
	SrCl	625–670
	SrOH	650–700
	Li (atomic emission)	610–670
Orange		550–640 (overall)
	CaOH	550–625
	CaCl	580–620
Yellow		570–600 (overall)
	Na (atomic emission)	589 (dominant sodium "d-line")
Green		500–570 (overall)
	BaCl	500–530
	BaOH	490–525
	CuOH	500–600
	BO_2	470–580 with 546 dominant[d,e]
Blue		415–550 (overall)
	CuCl	415–550
	CuBr	400–550[f]
	CuI	460–475[g]

[a] Meyerriecks and Kosanke (2003).
[b] Sabatini (2018).
[c] Douda, Theory of Colored Flame Production (1964).
[d] Young, et al. (2009).
[e] Poret and Sabatini (2013).
[f] Juknelevicious, et al. (2015).
[g] Klapötke, et al. (2014).

temperature of atomic species) or color quality will suffer. For example, green emitter BaCl is unstable above 2,000°C and the best blue emitter, CuCl, should not be heated above 1,200°C (Shidlovskiy 1964). A temperature *range* is therefore required, high enough to achieve the excited electronic state of the vaporized species but low enough to minimize dissociation.

5. The presence of incandescent solid or liquid particles in the flame will adversely affect color quality. The resulting "black body radiation" emission of white light will enhance *overall* light emission intensity, but the color *quality* will be diluted. A "washed out" color will be perceived by the viewers. The use of magnesium or aluminum metal in color compositions will yield high flame temperatures and high overall intensity, but broad emission from incandescent magnesium oxide or aluminum oxide products may lower color purity.
6. Every effort must be made to minimize the presence of unwanted atomic and molecular emitters in the flame. Sodium compounds, even as minor

impurities, must be avoided, or at least minimized, in any color mixtures except yellow. The intense yellow–orange atomic emission from sodium (589 nm) will overwhelm other colors.

A binder may be required in a colored flame mixture if the composition will be pelleted or formed into "stars." If so, the minimum percentage of binder should be used. Carbon-containing compounds can produce an orange flame color. The use of a binder that is already substantially oxidized (one with a high oxygen content, such as dextrine) can minimize this problem. Binders such as paraffin that contain little or no oxygen should be avoided unless a hot, oxygen-rich composition is being prepared.

OXIDIZER SELECTION

The numerous requirements for a good oxidizer were discussed in detail in Chapter 3. An oxidizer for a colored-flame composition must meet all of those requirements and in addition must either emit the proper wavelength light to yield the desired color or *not* emit any light that interferes with the color produced by other components. In addition, the oxidizer must react with the selected fuel to produce a flame temperature that yields the maximum emission of light in the proper wavelength range. If the temperature is too low, not enough "excited" molecules are produced and weak color intensity is observed. A flame temperature that is too hot may decompose the molecular emitter, destroying color quality.

Table 10.9 gives some data on flame temperatures obtained by Shimizu for oxidizer–shellac mixtures (T. Shimizu 1981). The data in Table 10.9 show that potassium nitrate, with its highly endothermic heat of decomposition, produces significantly lower flame temperatures with shellac than the other three oxidizers, and therefore the yellow light intensity from the sodium in the sodium oxalate will be substantially less for the potassium nitrate-based compositions.

In order to use potassium nitrate in bright-colored flame mixtures, it is usually necessary to include magnesium or magnalium as a fuel to raise the flame temperature. Potassium emits weak violet light (near 450 nm), but good red and green flames can be produced with potassium compounds present in the mixture (ammonium perchlorate is advantageous for color compositions because it contains no metal ion to interfere with color quality). A source of chlorine is also helpful for formation of volatile BaCl (green) or SrCl (red) emitters. The presence of chlorine in the flame also aids by hindering the formation of magnesium oxide and strontium or barium oxide, all of which will hurt the color quality. Shidlovskiy suggests a minimum of 15% chlorine donor in a color composition when magnesium metal is used as a fuel (Shidlovskiy 1964).

However, chlorine is not *necessary* in order to produce color flames. It has been shown that a series of colors—even the tricky blue color—can be produced successfully using nitrate oxidizers without the use of any metallic fuels or chlorine-containing compounds (Jennings-White, Nitrate colors 1993). The use of chlorine-containing compounds and metal fuels, however, does aid in expanding the burn rate range for color compositions and in expanding the range of flame temperatures that can be achieved with color compositions.

TABLE 10.9
Flame Temperatures for Oxidizer–Shellac Mixtures[a]

	Flame Temperatures for Various Oxidizers (°C)			
Composition	Potassium Perchlorate, $KClO_4$	Ammonium Perchlorate, NH_4ClO_4	Potassium Chlorate, $KClO_3$	Potassium Nitrate, KNO_3
I. 75% Oxidizer 15% Shellac 10% Sodium oxalate	2,250	2,200	2,180	1,675
II. 70% Oxidizer 20% Shellac 10% Sodium oxalate	2,125	2,075	2,000	1,700
III. 65% Oxidizer 25% Shellac 10% Sodium oxalate	1,850	1,875	1,825	1,725

Sodium oxalate was added to yield a yellow flame color and permit temperature measurement by the "line reversal" method.

[a] T. Shimizu, Studies on strobe light pyrotechnic compositions (1982).

The best oxidizer to choose, therefore, should contain the metal ion whose emission, in atomic or molecular form, is to be used for color production, *if* such an oxidizer is commercially available, works well, and is safe to use. Using this logic, for example, the chemist would select barium nitrate or barium chlorate for green flame mixtures. Strontium nitrate, although hygroscopic, is frequently selected for red compositions. The use of a strontium compound that does not act as a primary oxidizer (e.g., strontium carbonate for red) may be required for hygroscopicity, burn rate, and safety considerations. However, these inert ingredients will tend to lower the flame temperature and therefore lower the emission intensity. If so, a metal fuel may be required to raise the flame temperature and offset this effect (see below). A lower percentage of color ingredients may also be required in such cases to produce a satisfactory color.

FUELS AND BURNING RATES

Applications involving colored-flame compositions will require either a long-burning composition or a mixture that burns rapidly to give a burst of color. Highway flares (fusees) and the "lances" used to create fireworks set pieces require long burning times ranging from 1 to 30 min. "Fast" fuels such as metal powders and charcoal are usually *not* included in these slow mixtures. Partially oxidized organic fuels such as dextrine can be used. Coarse oxidizers and fuel particles can also retard the burning rate. Highway flares often contain common sawdust as a coarse, slow-burning retardant and wax as a low-melting heat sink to help achieve lengthy burning times.

To achieve rapid burning, such as in the brightly colored "stars" used in aerial fireworks, compositions will contain charcoal or a metallic fuel. Fine particle sizes will be used, and all ingredients will be well-mixed to achieve a very homogeneous and fast burning, mixture.

Military color flare compositions have traditionally used magnesium as a fuel to maximize flame temperature and candlepower (Webster III 1985). When magnesium is used, however, moisture is always a concern. If compositions containing magnesium are not thoroughly dried in the manufacturing process, and end items are not well sealed, the storage lifetime of the end items will be adversely affected by slow oxidation of the magnesium. Burn rates will slow up and candlepower will decrease over time.

Fireworks color effects became noticeably brighter in the 1970s and 1980s, largely due to an innovation from China. The Chinese factories in the 1970s pioneered the use of magnalium alloy, Mg/Al, in color compositions. The alloy used in fireworks is typically a 50/50 ratio of the two metals and consists of a solution of Al_3Mg_2 dissolved in Al_2Mg_3 (Kosanke and Kosanke 2004) (T. Shimizu 1981). Magnalium "ages" much better than magnesium metal by itself in color compositions, and the lower amount of aluminum does not interfere with the production of color in the flame. The magnalium fuel raises the flame temperature significantly over nonmetallic color compositions, and an entire range of colors can now be produced using magnalium-based compositions.

THE VELINE COLOR SERIES

A series of color compositions based on a basic set of starting chemicals was developed by master pyrotechnician Robert Veline, who generously published his formulations for hobbyists (and others) to use. Table 10.10 contains the Veline color system, for both "pure" colors and for the wider range of colors that can be obtained by mixing the base colors (Veline 1989).

Veline wanted to create a system of color compositions with as little metal fuel as possible (notice the small amounts of magnalium used) that could be mixed in a variety of ways to create dozens of other colors at the mixer's interest. The Veline colors would not always produce the most intense colors compared to other singly engineered compositions discussed below, but the system is extremely useful for cost and safety considerations, as well as learning the basic principles of color theory as it relates to pyrotechnics.

COLOR INTENSIFICATION WITH CHLORINE

Chlorine, Cl, is one of the keys to the production of good red, green, and blue flames, and its presence is sometimes required in a pyrotechnic mixture to achieve a good output (and at a specific burn rate) of these colors.

Chlorine serves two important functions in a pyrotechnic flame:

1. Chlorine forms volatile chlorine-containing molecular species with the color-producing metals, ensuring a sufficient concentration of emitters in the vapor phase.

TABLE 10.10
The Veline Color Series

	Prime	Red	Orange	Green	Blue
Red Gum		9	9	5	9
Charcoal	20				
Magnalium	5	6	6	11	6
Potassium perchlorate	55	55	55	30	55
Barium nitrate				24	
Red iron oxide	5				
Strontium carbonate		15			
Calcium carbonate			15		
Barium carbonate				15	
Copper carbonate					15
Parlon		15	15	15	15
Wood meal (70 mesh)	6				
Dextrine	+4	+4	+4	+4	+4
Composite Colors (Made by Mixing the Percentages of the Prime Colors Above)					
Yellow			45	55	
Chartreuse			20	80	
Aqua				80	20
Turquoise				55	45
Magenta	50				50
Maroon	85				15
Peach	25	60			15
Purple	15	5			80

2. These chlorine-containing species in the vapor phase are good emitters of narrow bands of visible light, producing the observed flame color.

Without both of these properties—volatility and light emission—good colors would be much more difficult to achieve.

The use of chlorate or perchlorate oxidizers ($KClO_3$, $KClO_4$, etc.) is one way to introduce chlorine atoms into the pyrotechnic flame. Another method is to incorporate a chlorine-rich organic compound into the mixture. Table 10.11 lists some for the chlorine donors commonly used in pyrotechnic mixtures. A dramatic increase in color quality can be achieved by the addition of a small percentage of one of these materials into a mixture. Shimizu recommends the addition of 2%–3% organic chlorine donor into compositions that don't contain a metallic fuel, and the addition of 10%–15% chlorine donor into the high-temperature mixtures containing metallic fuels (T. Shimizu 1981).

With magnesium-containing compositions, chlorine serves a third important function in pyrotechnic flame for color production. Shimizu attributes much of the value of these chlorine donors in magnesium-containing compositions to the production, in the flame, of hydrogen chloride, HCl, which reacts with magnesium oxide

TABLE 10.11
Chlorine Donors for Pyrotechnic Mixtures

Material	Formula	Melting Point (°C)	% Chlorine by Weight
Polyvinyl chloride (PVC)	$(\text{-CH}_2\text{CHCl-})_n$	Softens ca. 80, decomposes ca. 160	56
"Parlon" (chlorinated polyisopropylene)	–	Softens 140	ca. 66
Hexachlorobenzene	C_6Cl_6	229	74.7
"Dechlorane" (hexachloropentadiene dimmer)	$C_{10}Cl_{12}$	160	78.3
Hexachloroethane	C_2Cl_6	185	89.9

to form volatile MgCl molecules. Since free magnesium is taken up by chlorine and not oxygen, the incandescent emission from MgO particles is thereby reduced by the reaction

$$MgO + HCl \rightarrow MgCl + OH \tag{10.2}$$

and color quality improves significantly.

Red Flame Compositions: Classic Strontium-Based Systems

Classically, the best flame emission in the red region of the visible spectrum is produced by molecular strontium monochloride, SrCl. This species, unstable at room temperature, is generated in vapor phase in the pyrotechnic flame by a reaction between strontium and chlorine atoms. Strontium(II) chloride, $SrCl_2$, would appear to be a logical precursor to SrCl, and it is readily available commercially, but it is much too hygroscopic to be of practical use in pyrotechnic mixtures.

The SrCl molecule emits a series of bands in the 620–680 nm region, the "deep red" portion of the visible spectrum (other peaks are also observed). Strontium monohydroxide, SrOH, is another substantial emitter in the red and orange–red regions (Douda, *Theory of Colored Flame Production* 1964) (Kosanke and Kosanke 2004). The emission spectrum of a red flare is shown in Figure 10.1.

Strontium nitrate, $Sr(NO_3)_2$, is often used as a combination oxidizer/color source in red flame mixtures. A "hotter" oxidizer, such as potassium perchlorate, is frequently used in addition to help achieve higher temperatures and faster burning rates, as well as introduce chlorine to the system. Strontium nitrate, notably, is rather hygroscopic, and therefore water should not be used to moisten a binder for mixtures using this oxidizer. Strontium carbonate is much less hygroscopic and can give a beautiful red flame under suitable conditions. However, it contains an, essentially, pyrotechnically-inert anion, the carbonate ion CO_3^{2-}. Low percentages of this chemical should be used to avoid burning difficulties.

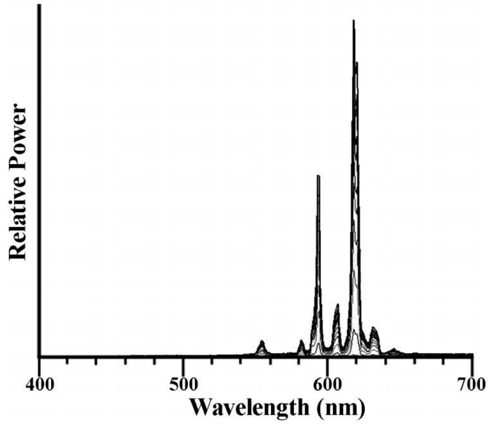

FIGURE 10.1 Emission spectrum of a red flare. Emission is concentrated in the 600–650 nm region. The primary emitting species are SrCl and SrOH molecules in the vapor state.

To keep the SrCl from further oxidizing to SrO in the flame, Shidlovskiy recommends using a composition containing a negative oxygen balance (excess fuel). Such a mixture will minimize the reaction

$$2\mathrm{SrCl} + \mathrm{O}_2 \rightarrow 2\mathrm{SrO} + \mathrm{Cl}_2 \quad (10.3)$$

and enhance color quality (Shidlovskiy 1964).

Notably, recent advances with the study of periodates have found some success in replacing perchlorates with periodates, presumably to generate SrI in the pyrotechnic flame. Sabatini reports that replacing 10.3% by weight potassium perchlorate with 5% by weight potassium periodate in a military red-light illuminating composition finds a comparable burn time, similar dominant wavelength and spectral purity, and even an increased luminous intensity (Sabatini, A Review of Illuminating Pyrotechnics 2018).

Additionally, use of the high-nitrogen-content organic molecule 5-aminotetrazole (5-AT, Figure 3.1) has been explored as an alternative to perchlorate-based systems. Sabatini and Moretti report that a strontium-nitrate-based system that replaces potassium perchlorate with 5-AT exhibits a similar burn time, increased light output, similar dominant red wavelength output, and increased overall spectral purity (Sabatini and Moretti 2013).

Several red formulas are presented in Table 10.12, and a magnesium-containing U.S. Navy flare formula for red is shown in Table 10.17 (along with green and yellow).

RED FLAME COMPOSITIONS: LITHIUM-BASED ALTERNATIVES

In addition to strontium, lithium-based compounds are also known to emit red light through the atomic emission of lithium (similar to the yellow sodium-based emission). Although not investigated as thoroughly as strontium, lithium-containing compositions *should* provide good red emission: The main lines of lithium are

TABLE 10.12
Red Flame Compositions

Composition		% by Weight	Use	Reference
I.	Ammonium perchlorate, NH_4ClO_4	70	Red torch	Shimizu, T. in R. Lancaster (1972)
	Strontium carbonate, $SrCO_3$	10		
	Wood meal (slow fuel)	20		
II.	Potassium perchlorate, $KClO_4$	67	Red fireworks star	Shimizu, T. in R. Lancaster (1972)
	Strontium carbonate, $SrCO_3$	13.5		
	Pine root pitch	13.5		
	Rice starch	6		
III.	Potassium perchlorate, $KClO_4$	32.7	Red fireworks star	Winokur (1978)
	Ammonium perchlorate, NH_4ClO_4	28.0		
	Strontium carbonate, $SrCO_3$	16.9		
	Red gum	14.0		
	Hexamethylenetetramine, $C_6H_{12}N_4$	2.8		
	Charcoal	1.9		
	Dextrine (dampen with 3:1 water:alcohol	3.7		
IV.	Potassium perchlorate, $KClO_4$	44	Red signal flare (very little residue)	Unpublished
	Strontium nitrate, $Sr(NO_3)_2$	31		
	Epoxy (fuel/binder)	25		
V.	Lithium perchlorate, $LiClO_4$	75	Lance	Koch (2001)
	Hexamine, $C_5H_{12}N_4$			
VI.	Ammonium perchlorate, NH_4ClO_4	49.5	Red star	Koch (2001)
	Dihydrazinotetrazine (DHT), $C_2H_6N_8$	49.5		
	Lithium carbonate, Li_2CO_3	1.0		
VII.	Strontium nitrate, $Sr(NO_3)_2$	43	"Green pyrotechnics" perchlorate-free red illuminant, replacement for U.S. military M662	Sabatini (2018)
	Magnesium 30/50 mesh, Mg	32		
	Polyvinyl chloride, PVC	15		
	Potassium periodate, KIO_4	5		
	Epoxy binder	5		

(*Continued*)

TABLE 10.12 (*Continued*)
Red Flame Compositions

Composition		% by Weight	Use	Reference
VIII.	Strontium nitrate, $Sr(NO_3)_2$	33.3	"Green pyrotechnics" perchlorate-free red illumant based on 5-aminotetrazole	Sabatini and Moretti (2013)
	Magnesium, 30/50 mesh, Mg	41.4		
	Polyvinyl chloride, PVC	14.7		
	5-aminotetrazole, CH_3N_5	3.8		
	Epon 813/Versamid 140 (binder)	6.8		

reported to be 610 and 670 nm, in similar ranges as strontium-based compounds (Koch, Evaluation of Lithium Compounnds as Color Agents for Pyrotechnic Flames 2001). Compositions based on readily available lithium perchlorate ($LiClO_4$) and lithium carbonate (Li_2CO_3) are shown in Table 10.12. One drawback to lithium compounds is their relatively high hygroscopic nature, which will of course cause issues with burning and long-term storage.

Based on thermodynamic calculations and other chemical considerations, evaluation by Koch suggests several rules for good lithium-based compositions (Koch, Evaluation of Lithium Compounnds as Color Agents for Pyrotechnic Flames 2001):

- Prepare fuel-rich compositions to avoid oxygen surplus and generation of undesirable LiOH compounds (which do not emit red like atomic Li will);
- Use fuels with a high hydrogen content to convert the undesirable LiOH in flames to gaseous lithium and water, H_2O;
- Avoid halogens, especially chlorine, which can generate LiCl that does not emit in the visible region (alternatively, the introduction of aluminum can "scavenge" halogens in pyrotechnic reactions).

Unlike barium, strontium (at the time of this publication) has not yet been designated an element of concern or one that requires further regulation for toxic environmental side effects, so the study of lithium-based red flame compositions has not had the same "green pyrotechnics" push as barium-based green flame compounds.

GREEN FLAME COMPOSITIONS: CLASSIC BARIUM-BASED SYSTEMS

Pyrotechnic compositions containing a barium compound and a good chlorine source can generate barium monochloride, BaCl, in the flame and the emission of green light will be observed. BaCl, an unstable species at room temperature, but is an excellent emitter in the 505–535 nm region of the visible spectrum, the "deep green" portion (Douda, *Theory of Colored Flame Production* 1964) (Kosanke and Kosanke 2004). The emission spectrum of a green flare was shown in Figure 4.1.

Notably, barium and strontium are chemically very similar, with barium one row down from strontium on the periodic table. They are found in nature together and it is difficult to remove all traces of strontium from nature barium sources, or vice-versa. Emission spectra with sufficient sensitivity will occasionally show a minor 620–680 nm strontium emission in a barium-based mixture or 505–535 nm barium emission in a strontium mixture, if the chemical has not been purified completely.

Barium nitrate, $Ba(NO_3)_2$, and barium chlorate $Ba(ClO_3)_2$, are used most often to produce green flames, serving both as the oxidizer and color source. Barium chlorate can produce a deep green flame, but it is somewhat unstable (and acid sensitive) and can form explosive mixtures with good fuels. Barium nitrate produces an acceptable green color, and it is considerably safer to work with due to its high decomposition temperature and endothermic heat of decomposition. Barium carbonate, $BaCO_3$, is another possibility, but (similar to strontium carbonate stated above) it must be used in low percentage due to its effectively pyrotechnically inert anion, CO_3^{2-}.

An oxygen-deficient flame is required for a good-quality green flame. Otherwise, barium oxide (BaO) will form and emit a series of bands in the 480–600 nm range, yielding a dull, yellowish-green color. The reaction

$$2BaCl + O_2 \rightarrow 2BaO + Cl_2 \tag{10.4}$$

will shift to the left-hand side when chlorine is present in abundance and oxygen is scarce, and a good green color will be achieved. A flame temperature that is too high will decompose BaCl, however, so metal fuels must be held to a minimum, if they are used at all.

This temperature dependence and the value of a chlorine source are important to remember. A binary mixture of barium nitrate and magnesium or magnalium metal will produce a brilliant *white* light upon ignition (found intentionally in some handheld sparklers), from a combination of MgO and BaO emission at the high temperature achieved by the mixture. Addition of a chlorine-containing organic fuel to lower the temperature and provide chlorine atoms to form BaCl can produce a green flame. Several green flame compositions are given in Table 10.13, and a magnesium-containing U.S. Navy flare formula for green is shown in Table 10.17 (along with red and yellow).

Additionally, and similar to strontium/red-flame research noted previously, use of the high-nitrogen-content organic molecule 5-aminotetrazole (5-AT, Figure 3.1) has been explored as an alternative to perchlorate-based systems, while still retaining barium as the primary green-color emitter. Sabatini and Moretti report that a barium-nitrate-based system that replaces potassium perchlorate with 5-AT exhibits a similar burn time, slightly increased light output, similar dominant green wavelength output, and similar overall spectral purity (Sabatini and Moretti 2013).

TABLE 10.13
Green Flame Compositions

Composition		% by Weight	Use	Reference
I.	Ammonium perchlorate, NH_4ClO_4	50	Green torch	Shimizu, T. in R. Lancaster (1972)
	Barium nitrate, $Ba(NO_3)_2$	34		
	Wood meal	8		
	Shellac	8		
II.	Barium chlorate, $Ba(ClO_3)\cdot 2H_2O$	65	Green torch	Unpublished
	Barium nitrate, $Ba(NO_3)_2$	25		
	Red Gum	10		
III.	Potassium perchlorate, $KClO_4$	46	Green fireworks star	Shimizu, T. in R. Lancaster (1972)
	Barium nitrate, $Ba(NO_3)_2$	32		
	Pine root pitch	16		
	Rice starch	6		
IV.	Barium nitrate, $Ba(NO_3)_2$	59	Russian green flare	Shidlovskiy (1964)
	Polyvinyl chloride	22		
	Magnesium	19		
V.	Barium nitrate, $Ba(NO_3)_2$	43	“Green pyrotechnics” perchlorate-free green-flame emitter.	Sabatini and Moretti (2013)
	Magnesium 30/50 mesh, Mg	32		
	Polyvinyl chloride, PVC	15		
	5-aminotetrazole, CH_3N_5	5		
	Epon 813/Versamid 140 (binder	5		
VI.	Potassium nitrate, KNO_3	83	“Green Pyrotechnics” boron-based green flame	Poret and Sabatini (2013)
	Amorphous boron, B	10		
	Epon 828/Epikure 3140 (binder)	7		
VII.	Potassium nitrate, KNO_3	83	“Green Pyrotechnics” boron carbide-based green flame	Brinck (2014)
	Boron carbide, B_4C	10		
	Epon 828/Epikure 3140 (binder)	7		
VIII.	Magnesium diboride, MgB_2	21	“Green Pyrotechnics” magnesium diboride-based green flame	Brusnahan, et al. (2016)
	Potassium nitrate, KNO_3	73		
	Polyvinyltetrafluoroethylene, PTFE	3		

GREEN FLAME COMPOSITIONS: "GREEN PYROTECHNICS" WITH BORON-BASED COMPOSITIONS

While the generation of BaCl has been the favored method of producing green flames, both the presence of barium and chlorine donors—such as perchlorate—are problematic in "green pyrotechnics" due to the probable cardiotoxicity of barium and the toxicity issues of perchlorate to proper human thyroid operation. Alternative chlorine donors, such as polyvinyl chloride, PVC, have been evaluated in barium-based compounds.

Recent studies with both elemental boron (B) and boron carbide (B_4C) have shown promising results in generating green flames, removing both the barium and perchlorate issue. Metastable boron dioxide, BO_2, is expected to the primary emitter of the green color at 546 nm. Poret and Sabatini report a KNO_3/B/Epon 828 (binder) formulation with a 567 nm dominant wavelength and a "spectral purity" of 55.0%, as compared to the control $Ba(NO_3)_2$/Mg/PVC/Laminac (binder) formulation showing a 562 nm dominant wavelength and overall 66.4% spectral purity (noting that the spectral purity difference may not be visible to the naked eye) (Poret and Sabatini 2013). The drawbacks in this boron-based composition is that it burned 3–4 times as fast and approximately 800°C hotter, which may be undesirable for compositions that intend to be longer burning such as for lance or star fireworks. Similar work evaluated using *crystalline* boron in addition to amorphous boron in this composition, which was found to prolong the burn time, although simultaneously decrease overall luminous intensity (Sabatini, Poret and Broad, Use of Crystalline Boron as a Burn Rate Retardant toward the Development of Green-Colored Handheld Signal Formulations 2011).

Follow-on research with boron carbide formulations mitigated this burn rate issue in a KNO_3/B_4C/Epon 828 (binder) mixture which showed similar burn time to the barium-based mixture, a 561 nm dominant wavelength, 51.96% spectral purity, and a comparable luminous intensity (Brinck 2014).

The metastable BO_2 free radical species, noted above as being a viable green-light emitter, has also been produced through employing magnesium diboride—MgB_2—as fuel and boron source. Brusnahan et al. report that using magnesium diboride with either potassium nitrate or ammonium perchlorate (along with various binders and additives) provided very acceptable results (Brusnahan, et al. 2016). While a brief search of chemical retailers, at the time of this writing, did not find the chemical to be inexpensive for large bulk use, it is a common enough used material in the semiconductor industry that could allow for reduced costs, if the market required.

Some "green" boron-based green flame compositions are shown in Table 10.13.

BLUE FLAME COMPOSITIONS: CLASSIC COPPER CHLORIDE-BASED SYSTEMS

The generation of an intense, deep-blue flame represents the ultimate challenge to the pyrotechnic chemist. A delicate balance of temperature and molecular behavior is required to obtain a good blue, but it can be done if the conditions are right.

The best flame emission in the blue region of the visible spectrum (435–480 nm) is obtained from copper monochloride, CuCl. Flame emission from this molecular species yields a series of bands in the region from 428 to 452 nm, with additional peaks between 476 and 488 nm (Douda, *Theory of Colored Flame Production* 1964) (Kosanke and Kosanke 2004).

In an oxygen-rich flame, and at temperatures above 1,200°C, CuCl is unstable and will react to form CuO and CuOH. CuOH emits in the 525–555 nm region (green!) and substantial emission may overpower any blue effect that is also present. Copper oxide, CuO, emits a series of bands in the red region, and this reddish emission is often seen at the top of blue flames, where sufficient oxygen from the atmosphere is present to convert CuCl to CuO (T. Shimizu 1981). Control of the presence of chlorine and limiting the flame temperature is crucial in these systems to generate a deep blue color.

Copper acetoarsenite, $(CuO)_3As_2O_3{\cdot}Cu(C_2H_3O_2)$, also known as "Paris Green," was widely used in blue flame mixtures until a few decades ago. It produces a good blue flame, but it has vanished from commercial formulas because of the health hazards associated with its use (the arsenic being toxic to humans and animals).

Copper oxide (CuO), basic copper carbonate $[CuCO_3{\cdot}Cu(OH)_2]$, and copper sulfate—available commercially as $CuSO_4{\cdot}5H_2O$—are among some of the common materials used in blue flame mixtures. Potassium perchlorate and ammonium perchlorate are the oxidizers found in most blue compositions. Potassium chlorate *would* be an ideal choice because of its ability to sustain reaction at low temperatures (remember, CuCl is unstable above 1,200°C). However, in the presence of moisture, the chlorate anion can undergo "salt metathesis" and move from potassium to copper, forming copper chlorate, $Cu(ClO_3)_2$. Copper chlorate is an *extremely* reactive material, to the point of being readily explosive. The chance of it forming should a copper-based blue mixture get wet precludes the commercial use of $KClO_3$ or any chlorate source.

Several formulas for blue flame compositions are given in Table 10.14. An extensive review of blue and purple flames, concentrating on potassium perchlorate mixtures, has been published by Shimizu (T. Shimizu, Studies on blue and purple flame compositions made with potassium perchlorate 1980).

TABLE 10.14
Blue Flame Compositions

Composition		% by Weight	Use	Reference
I.	Potassium perchlorate, $KClO_4$	68.5	Blue flame- "excellent"	Shimizu (1980)
	Polyvinyl chloride	6		
	Copper oxide, CuO	15		
	Red Gum	7.5		
	Rice starch	+5%		
II.	Potassium perchlorate, $KClO_4$	40	Blue flame	Shimizu, T. in R. Lancaster (1972)
	Ammonium perchlorate, NH_4ClO_4	30		
	Copper carbonate, $CuCO_3$	15		

(*Continued*)

TABLE 10.14 (*Continued*)
Blue Flame Compositions

Composition		% by Weight	Use	Reference
	Red gum	15		
III.	Potassium perchlorate, $KClO_4$	68	Blue flame "excellent"	Shimizu (1980)
	Copper carbonate, $CuCO_3$	15		
	Polyvinyl chloride	11		
	Red gum	6		
	Rice starch	+5%		
IV.	Ammonium perchlorate, NH_4ClO_4	70	Blue fireworks star (with charcoal tail)	Stone (1977)
	Red gum	10		
	Copper carbonate, $CuCO_3$	10		
	Charcoal	10		
	Dextrine (moisten with isopropyl alcohol	+5%		
V.	Copper iodate, $Cu(IO_3)_2$	15	"Green pyrotechnics" chlorine-free blue flame, CuI emitter.	Klapötke, et al. (2014)
	Guanidinium nitrate, $CH_6N_4O_3$	50		
	Magnesium, Mg	10		
	Copper, Cu	15		
	Epon 828/Epikure 3140 (binder)	5		
VI.	Potassium iodate, KIO_3	56.8	"Green pyrotechnics" chlorine-free blue flame, CuI emitter	Koch (2015)
	Malachite, 2 $CuCO_3$-$Cu(OH)_3$	27.4		
	Sulfur, S_8	15.8		
VII.	Potassium bromate, $KBrO_3$	58	"Green pyrotechnics" chlorine-free blue flame, CuBr emitter	Juknelevicious, et al. (2015)
	Copper(I) bromide, CuBr	18		
	Ammonium bromide, NH_4Br	12		
	Hexamine, $C_6H_{12}N_4$	12		
VIII.	Potassium bromate, $KBrO_3$	68	"Green pyrotechnics" chlorine-free blue flame, CuBr emitter	Koch (2015)
	Malachite, 2 CCO_3-$Cu(OH)_3$	15		
	Sulfur, S_8	17		

Material in Composition IV is actually basic copper carbonate, 2 $CuCO_3 \cdot Cu(OH)_2$.

BLUE FLAME COMPOSITIONS: "GREEN PYROTECHNICS" WITH COPPER IODIDE AND COPPER BROMIDE

As noted above, generation of the CuCl species produces an excellent blue flame, though that typically requires a chlorine source such as perchlorate, known to have environmental concerns as discussed previously. Furthermore, CuCl is an unstable species in flame and too high of a flame temperature can decompose the fleeting molecule, washing out the intended blue color and creating copper(II) oxide, which emits a red color. Research undertaken by Klapötke et al. suggested that a copper(I) iodide—CuI—could prove to be an equally suitable, or superior, blue-flame emitter (Klapötke, Rusan and Sabatini 2014). Whereas CuCl emits in the 435–480 nm blue region, CuI was suggested to emit around 460 nm. Copper(II) iodate—$Cu(IO_3)_2$—served as the oxidizer along with magnesium, guanidinium nitrate, and either urea or metallic copper to burn and generate the CuI species in the flame for emission. Performance was shown to be equal to, or even superior to, that of the CuCl emitting reference composition. Copper iodate is still prohibitively expensive for pyrotechnic compositions based on current market prices, but the research showing that successful chlorine-free copper-based blue-light emitters can be used in energetic materials is a significant advancement in the "greening" of pyrotechnics.

Another halogen, bromine, has been investigated as another alternative to chlorine, in this case generating copper bromide, CuBr, in pyrotechnic flame. This can be achieved in a process similar to the above by synthesizing copper bromate—$Cu(BrO_3)_2$—and generating CuBr as a dissociation product or by creating CuBr in the flame by having a bromine donor in the presence of copper, such as using copper metal with potassium bromate, $KBrO_3$, or ammonium bromide, NH_4Br (the latter of which is known to be a "coolant" in pyrotechnic compositions) (Juknelevicious, et al. 2015). The dominant wavelength of CuBr is expected to be 473 nm, right in the middle of the blue color spectrum range. While copper bromate isn't widely available, pricing on potassium bromate as an oxidizer/bromine donor in copper-based formulations was found to be (at the time of this writing) about 35% more expensive in bulk than potassium perchlorate, not prohibitively expensive but another consideration for the pyrotechnic chemist.

Koch undertook a holistic evaluation of CuX emitters, where X is a halogen F, Cl, Br, or I. While CuF was found to be a poor blue emitter, CuCl, CuBr, and CuI were all found to have variable utility as blue-flame emitters. Formulations for CuI- and CuBr-based blue-color emitters are shown in Table 10.14.

PURPLE FLAME COMPOSITIONS

A purple flame, the relative "newcomer" to pyrotechnics, can be achieved by the correct balance of red and blue emitters. The additive blending of these two colors produces a range of colors in the purple–lilac–violet–magenta family as perceived by the observer. Several comprehensive review articles on purple flames have been published. The compositions given in Table 10.15 received an "excellent" rating in the review article written by Shimizu (T. Shimizu, Studies on blue and purple flame compositions made with potassium perchlorate 1980).

TABLE 10.15
Purple Flame Compositions (Shimizu 1980)

Composition		% by Weight	Comment
I.	Potassium perchlorate, $KClO_4$	70	"Excellent"
	Polyvinyl chloride	10	
	Red gum	5	
	Copper oxide, CuO	6	
	Strontium carbonate, $SrCO_3$	9	
	Rice starch	+5%	
II.	Potassium perchlorate, $KClO_4$	70	"Excellent"
	Polyvinyl chloride	10	
	Red gum	5	
	Copper powder, Cu	6	
	Strontium carbonate, $SrCO_3$	9	
	Rice starch	+5%	

As noted previously, potassium is a weak emitter of purple color but generally not sufficient enough for colored-flame pyrotechnics. Shimizu reports that the emission is actually strong in the *ultraviolet* region, but that is not visible to the human eye (T. Shimizu, Fireworks from a Physical Standpoint, Part Two 1983).

YELLOW FLAME COMPOSITIONS: SODIUM

A yellow–orange flame color is easily achieved by atomic emission from sodium. The emission intensity at 589 nm *increases* as the reaction temperature is raised, and there is no molecular emitting species here to decompose at higher temperatures. Ionization of sodium atoms to sodium ions will occur at very high temperatures, however, so even here there is an upper limit of temperature that must be avoided for maximum color quality.

A more pure "canary yellow" can be achieved pyrotechnically by blending green and orange. Pyrotechnic compositions that contain a barium compound (for green emission) and a calcium or sodium compound for yellow–orange color can achieve some beautiful color effects in the "yellow" region. Trial and error is probably the best method to use in finding the "perfect" mix for a desired yellow hue.

Most sodium compounds tend to be quite hygroscopic, and therefore for simple compounds such as sodium nitrate ($NaNO_3$), sodium chlorate ($NaClO_3$), and sodium perchlorate ($NaClO_4$), combining the oxidizing anion with the metallic emitter *cannot* be used unless precautions are taken to protect against moisture before, during, and after the manufacturing process. Sodium oxalate ($Na_2C_2O_4$) and cryolite (Na_3AlF_6) are lower in hygroscopicity and they are therefore the color agents used in most commercial yellow flame mixtures. Some representative yellow compositions are given in Table 10.16, and a U.S. Navy flare formula for yellow is shown in Table 10.17 (along with red and green).

TABLE 10.16
Yellow Flame Compositions

Composition	% by Weight	Use	Reference
I. Potassium perchlorate, $KClO_4$	70	Yellow fireworks star	Shimizu, T. in R. Lancaster (1972)
Sodium oxalate, $Na_2C_2O_4$	14		
Red gum	6		
Shellac	6		
Dextrine	4		
II. Potassium perchlorate, $KClO_4$	75	Yellow fire	Shimizu, T. in R. Lancaster (1972)
Cryolite, Na_3AlF_6	10		
Red gum	15		
III. Sodium nitrate, $NaNO_3$	56	Russian yellow fire	Shidlovskiy (1964)
Magnesium	17		
Polyvinyl chloride	27		
IV. Potassium nitrate, KNO_3	37	Russian yellow fire	Shidlovskiy (1964)
Sodium oxalate, $Na_2C_2O_4$	30		
Magnesium	30		
Resin	3		
V. Barium nitrate, $Ba(NO_3)_2$	17	Yellow flare	McIntyre (1980)
Strontium nitrate, $Sr(NO_3)_2$	16		
Potassium perchlorate, $KClO_4$	17		
Sodium oxalate, NaC_2O_4	17		
Hexachlorobenzene, C_6Cl_6	12		
Magnesium	18		
Linseed oil	3		

SODIUM IMPURITIES: A CAUTION IN COLOR PRODUCTION

It must be remembered that a little bit of sodium goes a long way in affecting flame color, due to the fact that sodium is an atomic, rather than a molecule emitter. A molecular emitter must form in the flame via a reaction between two chemical species. An atomic emitter requires no such flame chemistry to vaporize the atomic material, and it is ready to emit its atomic spectrum immediately upon vaporization in the pyrotechnic flame. As such, even a low percentage of a sodium impurity in a bulk chemical can cause that chemical to affect flame color to a significant extent. Quality control of raw materials is important when the production of a pure color is the goal, especially with sodium impurities.

TABLE 10.17
U.S. Navy Flare Formulas (Webster III 1985)

	% by Weight		
Material	**Red**	**Green**	**Yellow**
Magnesium	24.4	21.0	30.3
Potassium perchlorate, $KClO_4$	20.5	32.5	21.0
Strontium nitrate, $Sr(NO_3)_2$	34.7		
Barium nitrate, $Ba(NO_3)_2$		22.5	20.0
Polyvinyl chloride	11.4	12.0	
Sodium oxalate, $Na_2C_2O_4$			19.8
Copper powder, Cu		7.0	
Asphaltum	9.0		3.9
Binder		5.0	5.0

ORANGE FLAME COMPOSITIONS: CALCIUM AND SODIUM/STRONTIUM COMBINATIONS

Calcium is the most common generator of orange color, with calcium chloride, CaCl, and calcium hydroxide, CaOH, as the main emitting species in pyrotechnic flame, with the monohydroxide as the preferred emitter due to its dominant 600 nm wavelength, vice 609 nm for the monochloride (Kosanke and Kosanke 2004). The most common calcium colorants for orange flame are calcium carbonate, $CaCO_3$, calcium oxalate, CaC_2O_4, and calcium sulfate, $CaSO_4$. The addition of varying amounts of strontium can also adjust the perceived color from orange to orange–red, depending on the purpose, and addition of barium compounds can adjust the color from yellow to yellow–green.

Notably, some compositions mixing yellow from sodium and red from strontium have been published showing good orange color production as well, being careful not to wash out the red color with too much sodium.

Some representative orange compositions are given in Table 10.18.

INFRARED EMISSION AND PYROTECHNICS

As the 20th century proceeded, and modern technology for the detection and analysis of the light output from pyrotechnics and other light-emitting articles continued to improve, interest on the military side moved from the visible into the infrared region of electromagnetic radiation.

Infrared radiation is emitted as a continuum from warm and hot objects (Military Pyrotechnic Series Part One, “Theory and Application” 1967), and it is also emitted in discrete wavelengths (or frequencies, which some scientists prefer to use to describe electromagnetic radiation) from molecular species in association with vibrational and rotational activity involving the chemical bonds in the molecules. Chemical bonds either absorb infrared radiation of the proper wavelength to undergo a transition from a ground state vibrational state to an excited state or the bonds are first thermally excited to a higher vibrational level and return to the ground state with the emission of a photon of infrared radiation. This emission of infrared radiation

TABLE 10.18
Orange Flame Compositions

Composition		% by Weight	Use	Reference
I.	Sulphur, S	14	Orange flame	Haarman (1996)
	Calcium carbonate, $CaCO_3$	34		
	Potassium chlorate, $KClO_3$	52		
II.	Potassium chlorate, $KClO_3$	40	Orange star	Haarman (1996)
	Sodium carbonate, Na_2CO_3	8		
	Strontium carbonate, $SrCO_3$	2		
	Charcoal, C	2		
	Red gum	12		
	Dextrin	5		
III.	Ammonium perchlorate, NH_4ClO_4	22	Orange illuminating star	Sturman (1990)
	Potassium perchlorate, $KClO_4$	22		
	Potassium dichromate, K_2CrO_4	4		
	Calcium oxalate, CaC_2O_4	15		
	Magnalium, Mg/Al	18		
	Red gum	5		
	Alloprene (chlorinated rubber)	9		
	Vinyl wallpaper paste (binder)	5		
	Water (for mixing)	+12%		

can be used to detect objects that are warmer than their background and thereby provides a means of targeting those warm objects.

Night vision technology is one application of this area of technology. The detection of diesel engines, jet engines, and other “hot spots” that stand out from their background is another area of very active research interest, and pyrotechnic articles have been used to provide protection for hot objects that might be detectable due to infrared emission and therefore be in harm’s way in a combat setting.

Infrared radiation ranges from 0.80 microns (or 800 nm—the long wavelength end of visible light) out to 300 microns, where the microwave region begins. Warm objects emit a thermal fingerprint of infrared radiation that is a function of temperature and the types of chemical bonds, if any, that are emitting the radiation. “Spikes” of intensity from molecular vibrational activity are superimposed on the continuum from “black body” radiation from solids and liquids.

Countermeasures that can be used to protect against a thermal detector include the following:

1. A pyrotechnic flare that emits a high-intensity output of visible and infrared radiation, to “dazzle” the detector.
2. Use of a pyrotechnic smoke, where the smoke particles absorb and scatter the radiation that is emitted by the warm “target” object, causing it to not be distinguishable from the background.

3. The use of multiple "decoys" that are emitting infrared radiation of a type and energy output that mimics what the detector is specifically looking for and thereby divert attention away from the target.

Many of the "countermeasure" technologies for the protection of aircraft from "heat-seeking" missiles for the past decades have relied on method #3 above. These technologies have employed on a pyrotechnic system consisting of magnesium fuel with polytetrafluoroethylene (PTFE, or "Teflon®") as the reactive system. Upon ignition of the composition, in a flare, the fluorine atoms are released from the carbon skeleton of the polymer at elevated temperature and react vigorously with the magnesium fuel to produce magnesium fluoride (MgF_2), with carbon produced as another reaction product (Kubota and Serizawa, Combustion Processes of Mg/TF Pyrotechnics 1987).

$$2\text{Mg} + \left(\text{CF}_2\text{CF}_2\right)_n \rightarrow 2\text{MgF}_2 + 2\text{C} + \text{heat} \tag{10.5}$$

In an effort to maintain the proper signature, the binder that is used with this technology is also a highly fluorinated species containing enough residual hydrogen atoms to be soluble in a solvent such as acetone. The trade name for the polymer is Viton®, and the resulting blend of magnesium, Teflon, and Viton is known in the industry as "MTV" composition. The mixture burns fast and hot and has also found some applications as an ignition composition (Koch 2002). Obviously, much of the specifics of these compositions have not been widely published by the U.S. military to avoid adversaries to defeat or exploit any weaknesses in these systems.

As factories geared up to produce this vital composition for the defense industry, a number of tragic accidents occurred involving ignition of the mix during the post-blending handling process. Investigations revealed that the composition had very unique electrostatic properties that resulted in the composition retaining an electrostatic charge that developed during the production process for a long period of time. Measures were instituted to help disperse the accumulated charge, and the material was allowed to sit for a longer-than-normal time after consolidation operations were performed, in an effort to help prevent manufacturing accidents with this critical material. The technology in this area continues to evolve as detection methods and countermeasures get more and more sophisticated.

LIGHT AND COLOR PRODUCTION: SUMMARY

The production of bright light is one of the hallmarks of pyrotechnics, and a variety of methods and chemicals can be employed to "dial in" the correct brightness, color, and properties to achieve the desired effect. A very hot-burning mixture with metal fuels is needed for bright white-light emission, while the flame temperature needs to be moderated and metal fuels limited in certain colored flames to avoid decay/oxidation of the molecular color-emitting species (such as SrCl for red). A careful balance of fuel, oxidizer, and other chemicals are necessary to attain the desired objective, but a wealth of tools and tactics are available to the pyrotechnic chemist to realize many numerous different pyrotechnic effects.

11 Smoke Production

GREEN SMOKE: Pyrotechnically generated smoke is used for civilian and military applications. Colored smokes, such as the green smoke shown here, are used for entertainment as well as for military applications. The smoke is produced by the sublimation of a volatile dye in a burning pyrotechnic composition. The temperature of the composition must be high enough to vaporize the dye but not be too hot that the dye molecules are destroyed and the color is lost.

> One doesn't normally think about smoke—those sooty ashy byproducts—as a pyrotechnician's desired goal. But humans have been using this peculiar effect of solid particles floating about together in air for signaling, for obscuring, and for entertaining for as long as we have been able to control even the simplest campfires…

INTRODUCTION

Most explosive and pyrotechnic reactions produce some or even significant quantities of smoke, whether or not this visible phenomenon was intended. Smoke can obscure colored flames, disrupt breathing, or cause cleanup issues the particles settle on the ground[1]. Therefore, attempts are often made to keep the production of smoke to a minimum in such mixtures, and active research and development efforts are underway around the world to produce low-smoke pyrotechnics (Chavez, et al. 1999). Smoke is normally a nuisance and, in a confined area, it can be undesirable and unhealthy.

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[1] Not just annoying to sweep up, but indoor pyrotechnics for ice hockey games can cause melting of the ice or disruption of the icy surface for players' skates.

But, if you are in an armored vehicle and someone is aiming a heat-seeking missile in your direction, a good cloud of the right smoke at the right time can be a true lifesaver. A variety of smoke-producing compositions are purposefully manufactured for use in daytime signaling and protective obscuration, as well as for amusement and entertainment purposes.

Two basic processes are used to create smoke clouds:

1. The dispersion of solid or liquid particles.
2. The re-condensation of vaporized material.

Materials can either be released slowly via a pyrotechnic reaction or they can instantaneously be scattered using an explosive bursting charge. Technically, a dispersion of fine solid particles in air is termed *smoke*, while liquid particles in air create a *fog*. A *smoke* is created by particles in the 10^{-5}–10^{-9} m range, while larger suspended particles create a *dust* (Shidlovskiy 1964). Pyrotechnic smoke compositions must meet all of the standard requirements for an acceptable energetic device (good performance, safety, storage, etc.) that have been discussed in previous chapters.

GENERATION AND DISPERSION OF SOLID PARTICLES

A variety of events that will lead to smoke production can occur in the pyrotechnic flame. Incomplete burning of an organic fuel will produce a black, sooty flame (mainly atomic carbon or carbon-heavy materials). A highly oxidized fuel such as a sugar is not likely to produce carbon. Materials such as naphthalene ($C_{10}H_8$) and anthracene ($C_{14}H_{10}$)—volatile solids with high-carbon content—are good candidates for soot production. Several mixtures that will produce black smokes are listed in Table 11.1.

TABLE 11.1
Black Smoke Compositions

Composition		% by Weight	Reference
I.	Potassium chlorate, $KClO_3$	55	Shidlovskiy (1964)
	Anthracene, $C_{14}H_{10}$	45	
II.	Potassium chlorate, $KClO_3$	45	Shidlovskiy (1964)
	Naphthalene, $C_{10}H_8$	40	
	Charcoal	15	
III.	Potassium perchlorate, $KClO_4$	56	Shimizu, T. in R. Lancaster (1972)
	Sulfur	11	
	Anthracene, $C_{14}H_{10}$	33	
IV.	Hexachloroethane, C_2Cl_6	62	Shimizu, T. in R. Lancaster (1972)
	Magnesium, Mg	16	
	Naphthalene (or anthracene)	23	

A good white smoke can be similarly obtained by the formation of zinc chloride, $ZnCl_2$, from a reaction between zinc metal and a chlorinated organic compound (the chlorine-containing species serves as the oxidizer, discussed further below). This product also has the unusual *benefit* of being hygroscopic: reaction products that strongly attract moisture in the air (such as $ZnCl_2$) will have an enhanced "multiplier" smoke effect in humid atmospheres, enhancing the full smoke/fog cloud. The burning of elemental phosphorus, producing phosphorus oxides, can also be used to create dense white smoke as the oxides attract moisture to form acids such as phosphoric acid, H_3PO_4.

VAPORIZATION OF VOLATILES

The heat from the reaction between an oxidizer and fuel can vaporize a co-mixed, but non-reacted, volatile ingredient (i.e., no *chemical* change occurring in the vaporized material, only a *phase* change). The vaporized component, part of the original mixture, then condenses as fine, solid particles upon leaving the reaction zone, and a smoke is created. Volatile organic dyes, ammonium chloride, and sulfur can be used to create smokes using this method.

Alternately, the pyrotechnic reaction can occur in a separate container, and the heat that is produced volatilizes a smoke-forming component contained in an adjacent compartment. The vaporization and dispersion of heavy oils to create white smoke can be accomplished using this technique[2].

In a combination of the above product-based and volatilization-based methods, a product of a pyrotechnic reaction may vaporize upon formation in the reaction zone and then subsequently condense as fine particles in air, creating a smoke. Potassium chloride (boiling point 1,407°C) produces smoke in many potassium chlorate and potassium perchlorate compositions although smoke is usually not a goal that is intentionally sought from these mixtures.

COLORED-SMOKE MIXES

OVERVIEW OF COLORED-SMOKE PRODUCTION

The generation of colored smoke by the volatilization of an organic dye is a fascinating pyrotechnic "Goldilocks" problem: The chemicals and conditions have to be just right. The military, commercial fireworks, and entertainment industries rely on this technique for the generation of copious quantities of brilliant colored smoke. The requirements for an effective colored-smoke composition include the following:

1. The mixture must produce *sufficient heat* to melt-and-vaporize or sublimate the pyrotechnically inert colored dye, as well as produce a sufficient volume of gas to disperse the dye into the surrounding atmosphere.
2. The mixture must ignite at a *low temperature* and continue to burn smoothly at a low temperature (well below 1,000°C). If the temperature is too high, the

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[2] While no pyrotechnics are used, vaporization of oils is how toy hobby trains generate smoke from the engine's smokestack.

organic dye molecules will decompose and the color quality as well as volume of the smoke will deteriorate. Metal fuels are not used in colored-smoke mixtures because of the high-reaction temperatures they produce.

3. Although a low-ignition temperature is required, the smoke mixture must be *stable toward ignition* during manufacturing and storage over the expected range of ambient temperatures.
4. The molecules creating the colored smoke must be of *low toxicity* (including low carcinogenicity). As noted previously, they must readily sublime without decomposition at the temperature of the pyrotechnic reaction to yield a dense smoke of good color quality (Chin and Borer 1982).

When requirements that include low-ignition temperature and reliable propagation of burning at low-reaction temperature are considered, the choice of oxidizer rapidly narrows to one candidate: potassium chlorate, $KClO_3$. The ignition temperature of potassium chlorate combined with sulfur or many organic fuels is below 250°C (as well as generates gaseous products to help disperse the dye). Good heat production is achieved with such mixtures, in part due to the exothermic decomposition of $KClO_3$ at a temperature below 400°C, forming KCl and oxygen gas.

A mixture consisting of 70% $KClO_3$ and 30% sugar ($C_{12}H_{22}O_{11}$) ignites near 220°C and has a heat reaction of approximately 0.8 kcal/g (Domanico 2008). Both chlorate-sulfur and chlorate-sugar mixtures are used in commercial and military colored-smoke compositions.

Sodium bicarbonate ($NaHCO_3$) is often added to $KClO_3$/S colored-dye mixtures for two purposes:

1. Sodium bicarbonate will neutralize any acidic impurities that might stimulate premature ignition of the composition.
2. Sodium bicarbonate acts as a coolant by decomposing endothermically to evolve carbon dioxide gas (CO_2), which further aids the system by dispersing the vaporized dye.

Magnesium carbonate ($MgCO_3$) is also used as a coolant, absorbing heat to decompose into magnesium oxide (MgO) and CO_2. Varying the amount of coolant can be used to help obtain the desired rate of burning and the correct reaction temperature; if a mixture burns too rapidly, more coolant should be added.

The ratio of oxidizer to fuel will also affect the amount of heat and gas that are produced. A stoichiometric mixture of $KClO_3$ and sulfur (Equation 11.1) contains a 2.55:1 ratio of oxidizer to fuel, by weight. Colored-smoke mixtures in use today contain ratio very close to this stoichiometric amount: the chlorate/sulfur reaction is not strongly exothermic but a stoichiometric mixture will generate the heat necessary to volatilize the dye.

$$2KClO_3 + 3S \rightarrow 3SO_2 + 2KCl \tag{11.1}$$

The reaction requires 71.9% potassium chlorate and 28.1% sulfur (by weight), a 2.55 to 1.00 ratio.

The reaction of potassium chlorate with a carbohydrate (e.g., lactose, $C_{12}H_{22}O_{11}$) will produce carbon monoxide (CO), carbon dioxide (CO_2), or a mixture depending on the oxidizer–fuel ratio. The balanced equations are given as Equations 11.2 and 11.3. (Lactose occurs as a hydrate—one water molecule crystallizes with each lactose molecule.)

CO_2 Production:

$$8KClO_3 + C_{12}H_{22}O_{11} \cdot H_2O \rightarrow 8KCl + 12CO_2 + 12H_2O \tag{11.2}$$

The reaction uses 73.1% potassium chlorate and 26.9% lactose hydrate by weight, a 2.72 to 1.00 ratio. The heat of reaction is 1.06 kcal/g (Shidlovskiy 1964).

CO Production:

$$4KClO_3 + C_{12}H_{22}O_{11} \cdot H_2O \rightarrow 4KCl + 12CO + 12H_2O \tag{11.3}$$

The reaction uses 57.6% potassium chlorate and 42.4% lactose hydrate (by weight), a 1.36 to 1.00 ratio. The heat of reaction is 0.63 kcal/g (Shidlovskiy 1964).

The amount of heat can be controlled by adjusting the $KClO_3$–sugar ratio. Excess oxidizer should be avoided as it will encourage oxidation of the dye molecules. The quantity (and volatility) of the dye will also affect the burning rate. The greater the quantity of dye used, the slower will be the burning rate since the dye is actually a diluent (i.e., a pyrotechnically inert chemical getting in the way of the combustion reaction) in these mixtures. Typical colored-smoke compositions contain 40%–60% dye by weight. Table 11.2 shows a variety of colored-smoke compositions. Note the use of potassium chlorate, sulfur or sugar as the fuel, and coolants in all mixtures.

TABLE 11.2
Color Smoke Compositions

Composition	% by Weight	Reference
Green smoke		McIntyre (1980)
Potassium chlorate, $KClO_3$	25.4	
Sulfur	10.0	
Green dye	40.0	
Sodium bicarbonate, $NaHCO_3$	24.6	
Red smoke		McIntyre (1980)
Potassium chlorate, $KClO_3$	29.5	
Lactose	18.0	
Red dye	47.5	
Magnesium carbonate, $MgCO_3$	5.0	
Yellow smoke		Smith and Stewart (1982)
Potassium chlorate, $KClO_3$	22.0	
Sucrose	15.0	
Chinoline yellow dye	42.0	
Magnesium carbonate, $MgCO_3$	21.0	

In colored-smoke compositions, the volatile organic dye melts/vaporizes or sublimes out of the reacting mixture and then condenses in air to form small solid particles. Structures for some of the dyes used in colored-smoke mixtures are given in Figure 11.1. The relatively complex bonding structure of these organic molecules leads to molecular orbitals where the electron transitions are just right to absorb wavelengths in the visible spectrum, leading to the reflection of other wavelengths and the appearance of color to the human eye.

To put it another way, the dyes are strong *absorbers* of visible light, and the light that is reflected off these particles is *missing* the absorbed wavelengths, and the *complementary* hue is perceived by observers. This color-producing process is different from that of colored-flame production, where the emitted wavelengths are perceived as color by the viewers. Table 10.7 lists the complementary colors for the various regions of the visible spectrum.

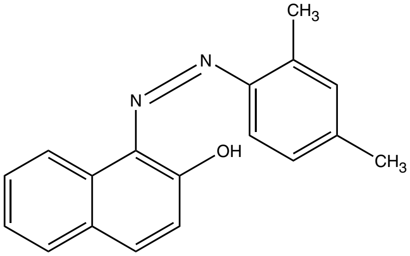
A variety of dyes have been used in colored-smoke mixtures; many of these dyes have been under investigation for carcinogenicity and other potential health hazards because of their molecular similarity to known "problem" compounds (Chin and Borer 1982) (Domanico 2008). The materials that work best in colored smokes have several properties in common, including the following:

1. *Volatility:* The dye must convert to the vapor state on heating, without substantial decomposition. Only low-molecular weight species (less than 400 g/mol) are usually used; volatility typically decreases as molecular weight increases. Salts do not work well, as ionic species generally have low volatility due to the strong inter-ionic attractions present in the crystalline lattice. Therefore, functional groups such as $–COO^-$ (carboxylate ion) and NR_4^+ (a substituted ammonium salt) cannot be present.
2. *Chemical Stability*: Oxygen-rich functional groups ($–NO_2$, $–SO_3H$) cannot be present to any significant extent. At the typical reaction temperatures of smoke compositions, these groups are likely to release their oxygen, leading to oxidative decomposition of the dye molecules. Groups such as $–NH_2$ and –NHR (amines) are used, but one must be cautious of possible oxidative coupling reactions that can occur in an oxygen-rich environment.

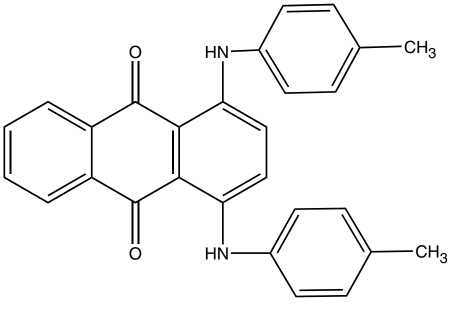
GREEN PYROTECHNICS: AN ENVIRONMENTALLY BENIGN YELLOW SMOKE

The complex organic chemical structure that gives colored dyes their "color" can also be the reason for their toxicity or having negative environmental effects. For example, Vat Yellow 4 shown in Figure 11.1 is listed as a "Group 3" chemical by the International Agency for Research on Cancer, meaning not yet classifiable as carcinogenic to humans but not yet determined to be *not* carcinogenic. This chemical was commonly used in military yellow smoke compositions, so research was undertaken to find a suitable alternative, one found with Solvent Yellow 33/D&C Yellow No. 11 (Moretti, et al. 2013). The formulation comparison between the in-service yellow smoke composition with Vat Yellow 4 and the new Solvent Yellow 33 is shown in Table 11.3. Both systems employ chlorate and sucrose as the binary pyrotechnic

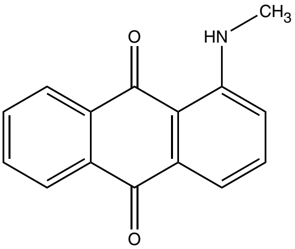
Orange 7
a-xylene-azo-b-naphthol



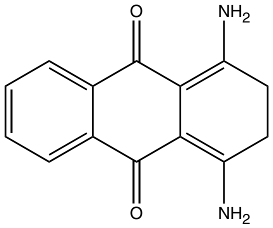
Solvent green 3
1,4-di-p-toluidino-anthraquinone



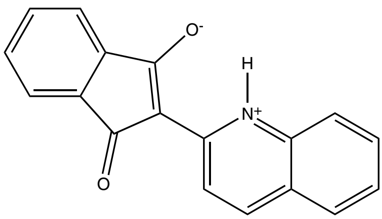
Disperse red 9
1-methylamino-anthraquinone



Violet
1,4-diamino-2,3-dihydroanthraquinone



Chinoline yellow
2-(2-quinolyl)-1,3-indandione



Vat yellow 4
dibenzo(a,h)pyrene-7,14-dione

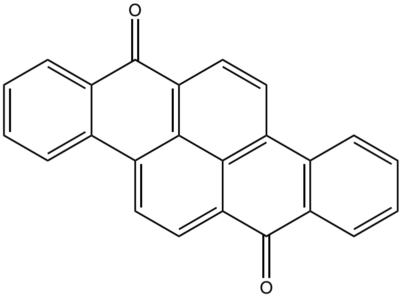


FIGURE 11.1 The chemical names and molecular structures of several dyes used in colored-smoke compositions. Smoke dyes must be stable at temperatures exceeding 200°C and must pass screening tests for carcinogenicity and other potential health hazards.

base, with other additives. Notably, the new "green" yellow dye composition not only meets the military requirements for burn time but also sensitivity testing shows a relatively insensitive composition as compared to military illuminating compositions. Additional research on this system investigated the "green" perchlorate replacement

TABLE 11.3
Comparison of Old and "Green" Military Yellow Smoke Compositions and Test Data

In-Service M194 Yellow Smoke		Proposed "Green" Replacement	
Ingredient	**% by Weight**	**Ingredient**	**% by Weight**
Vat Yellow 4 (yellow dye)	13	Solvent Yellow 33 (yellow dye)	37
Potassium chlorate	35	Potassium chlorate	34.5
Sucrose	20	Sucrose	21.5
Sodium bicarbonate (coolant)	3	Basic magnesium carbonate (coolant)	5.5
Benzanthrone (yellow dye)	28	Stearic acid (lubricant for processing)	1
VAAR binder	1	Fumed silica (assists in homogenous mixing)	0.5
Burn Time	9–18 s (requirement)		15.0 s
Burn Rate	3.89–7.78 g/s (requirement)		4.64 g/s
		Impact sensitivity (J)	17.2
		Friction sensitivity (N)	>360
		Spark sensitivity (J)	>0.25

5-aminotetrazole, 5-AT, as a gas-generating component that could aid in the dispersion of smoke particles for increased obfuscation (Gluck, et al. 2017).

WHITE SMOKE PRODUCTION

OVERVIEW OF WHITE SMOKE PRODUCTION

The processes used to generate white smoke by means of a pyrotechnic reaction include:

1. *Sublimation of sulfur, using potassium nitrate as the oxidizer:* A fuel-rich ratio of sulfur to KNO_3 is used in such mixtures, where the heat of the pyrotechnic reaction between sulfur and potassium nitrate will sublimate nearby sulfur. *Caution*: some toxic sulfur dioxide gas will be formed. Ignition and use of these mixtures must be done in a well-ventilated area[3].
2. *Combustion of phosphorus:* White or red phosphorus burns to produce various oxides of phosphorus, which then attract moisture to form dense white smoke. Research and development work relating to red phosphorus-based smoke mixtures is actively being pursued in the effort to find substitutes for the zinc chloride "HC" white smokes (see below). A typical red phosphorus

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[3] Though, notably, this process has been used for rodent control in closed areas such as indoor gardens.

mixture is given in Table 11.4. An explosive bursting charge is often used with the very-hazardous white phosphorus. *Caution*: Phosphorus-based smokes generate acidic compounds which may be irritating to the eyes, skin, and respiratory tract.

3. *Volatilization of oil:* A pyrotechnic reaction produces heat needed to vaporize high molecular weight hydrocarbons. The subsequent condensation of this oil in air creates a white smoke cloud. With proper selection of a low-toxicity oil, the negative health effects of this smoke are probably the least of all the materials discussed here.

TABLE 11.4
White Smoke Compositions

Composition		% by Weight	Note	Reference
I.	Hexachloroethane, C_2Cl_6	45.5	HC Type-C	Military Pyrotechnic Series Part One, "Theory and Application" (1967)
	Zinc oxide, ZnO	47.5		
	Aluminum	7.0		
II.	Hexachloroethane, C_2Cl_6	34.4	Modified HC	Military Pyrotechnic Series Part One, "Theory and Application" (1967)
	Zinc oxide, ZnO	27.6		
	Ammonium perchlorate, NH_4ClO_4	24.0		
	Zinc dust	6.2		
	Laminac	7.8		
III.	Red phosphorous	63	Animal studies have shown acute toxic effects of smoke products	McIntyre (1980)
	Butyl rubber, methylene chloride	37		
IV.	Red phosphorous	51.0		Smith and Stewart (1982)
	Magnesium	10.5		
	Magnesium dioxide, MgO_2	32.0		
	Magnesium oxide, MgO	1.5		
	Microcrystalline wax	5.0		
V.	Potassium nitrate, KNO_3	48.5	Contains arsenic	Lancaster (1972)
	Sulfur	48.5		
	Arsenic disulfide, As_2S_2	3.0		

4. Formation of zinc chloride (HC Smokes): A reaction of the type

$$CxCl_y + y/2Zn \rightarrow xC + y/2ZnCl_2 + \text{heat}$$

produces zinc chloride vapor, which condenses in air and attracts moisture to create a very effective white–gray smoke. These mixtures have been widely used for decades with an excellent safety record during the manufacturing process. However, $ZnCl_2$ can cause headaches and other possible health concerns upon continued human exposure, and replacements for the HC smokes are actively being sought due to the concerns relating to the various reaction products.

The original HC smoke mixtures (Type A) contained zinc metal and hexachloroethane (C_2Cl_6—the "HC" in HC Smokes), but this composition is *extremely* moisture-sensitive, igniting spontaneously, if moistened. An alternative approach involves adding a small amount of aluminum metal to the composition, and zinc oxide (ZnO) is used in place of the moisture-sensitive metal. Upon ignition, a sequence of reactions ensues of the type (Military Pyrotechnic Series Part One, "Theory and Application" 1967):

$$2Al + C_2Cl_6 \rightarrow 2AlCl_3 + 2C \quad (11.4)$$

$$2AlCl_3 + 3ZnO \rightarrow 3ZnCl_2 + Al_2O_3 \quad (11.5)$$

$$ZnO + C \rightarrow Zn + CO \quad (11.6)$$

$$3Zn + C_2Cl_6 \rightarrow 3ZnCl_2 + 2C \quad (11.7)$$

Alternatively, the original "trigger" reaction has been proposed to be (McLain 1980):

$$2Al + 3ZnO \rightarrow 3Zn + Al_2O_3 \text{ (a thermite-type process)} \quad (11.8)$$

In either event, the products are $ZnCl_2$, CO, and Al_2O_3, and the aluminum percentage in the composition will play a significant role in the overall burn rate. The zinc oxide cools and whitens the smoke by consuming atomic carbon in an endothermic reaction that occurs spontaneously above 1,000°C (Equation 11.6). The reactions with aluminum metal (Equations 11.4 or 11.8) are quite exothermic, and this heat evolution controls the burning rate of the smoke mixture. A minimum amount of aluminum metal will yield the best white smoke. Two "HC" smoke compositions are listed in Table 11.4.

5. *Cold Smoke*: White smoke can also be achieved by non-thermal means. A beaker containing concentrated hydrochloric acid placed near a beaker of concentrated ammonia will generate white smoke by the vapor–phase reaction

$$HCl(\text{gas}) + NH_3(\text{gas}) \rightarrow NH_4Cl(\text{solid})$$

Similarly, titanium tetrachloride ($TiCl_4$) rapidly reacts with moist air to produce a heavy cloud of titanium hydroxide—$Ti(OH)_4$—and HCl. Obviously, the hydrogen chloride gas that is produced will pick up moisture from the atmosphere to form hydrochloric acid, so this must be factored into decisions on where and how to deploy such a smoke cloud.

"GREEN PYROTECHNICS": HC SMOKE REPLACEMENT RESEARCH

A number of research programs have been carried out in recent years in efforts to develop white smoke screening compositions to replace HC smoke that are low in toxicity and meet all of the other requirements for a "good" pyrotechnic smoke. This has proven to be a difficult challenge because of the excellent obscuration that is provided by the HC smoke system.

One system that has been developed functions in a manner similar to the colored smokes, the volatilization pathway versus a combustion-product event. A volatile organic compound is vaporized/sublimated using a potassium chlorate/sulfur or potassium chlorate/sugar composition, and a white smoke cloud is produced. One of the chemicals that has proven to be effective at white smoke generation by this method is terephthalic acid, $C_8H_6O_4$, a material widely used in the chemical industry for the production of plastics. Because of this primary use, it is readily available in high purity and moderate in cost (recall that cost is always a major driver in pyrotechnic formulation selection). It sublimes readily at the potassium chlorate/sugar flame temperature to produce white smoke. The structure of terephthalic acid is shown in Figure 11.2.

A Terephthalic Acid "TA" Smoke Mixture

Potassium chlorate, $KClO_3$	23% by weight
Sucrose, $C_{12}H_{22}O_{11}$	14
Terephthalic acid, $C_8H_6O_4$	57
Magnesium carbonate, $MgCO_3$	3
Graphite	1
Nitrocellulose binder	2

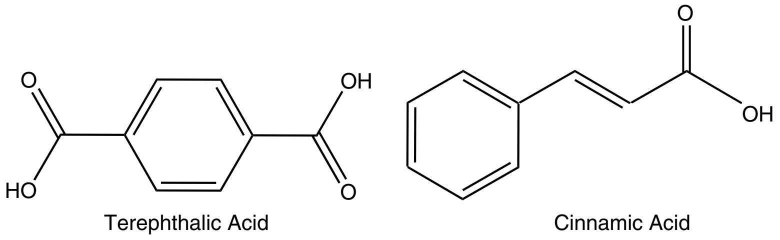

FIGURE 11.2 The chemical structures of terephthalic acid and cinnamic acid, both used for the production of low-toxicity white smoke by sublimation followed by re-solidification (deposition) in air.

While the TA smokes cannot match the HC smokes in obscuration on a pound-for-pound basis, it may well turn out to be the case that smoke devices for use in training will contain a low toxicity composition like the TA smoke mixture, and the more highly obscuring HC smokes are reserved for use in true battlefield conditions.

Recent research by Gluck et al demonstrated the use of the high-nitrogen content 5-aminotetrazole (5-AT, Figure 3.1) organic fuel for effective use in TA smoke compositions (Gluck, Klapotke and Shaw, Effect of Adding 5-Aminotetrazole to a Modifield U.S. Army Terephthalic Acid White Smoke Compositions 2017). Upon combustion, 5-AT produces significant nitrogen gas as a product, which may aid in spreading the volatilized terephthalic acid, increasing the obscuration effect. It was found that general substitution of sucrose as fuel (compared to the formula above) with 5-AT drastically reduced the "average transmittance" of light through the field by over half.

A similar HC-replacement smoke composition designed by the U.S. Navy is using cinnamic acid, $C_6H_5CHCHCO_2H$, another organic chemical used in the pharmaceutical, food, and perfume industries (Douda and Tanner 1977). Cinnamic acid has a substantially lower toxicity than HC smokes and is even used as a flavoring agent for human consumption. The structure of cinnamic acid is shown in Figure 11.2.

A Cinnamic Acid Smoke Mixture

Sucrose, $C_{12}H_{22}O_{11}$	12% by weight
Potassium chlorate, $KClO_3$	29
Sodium bicarbonate, $NaHCO_3$	6.5
Cinnamic acid, $C_6H_5CHCHCO_2H$	47.5

Finally, boron carbide—B_4C—has also shown promise as an environmentally friendly fuel for white smoke production. The boron carbide-based mixture designed by the U.S. Army (Shaw, et al. 2013):

Boron carbide, B_4C	13% by weight
Potassium nitrate, KNO_3	60
Potassium chloride, KCl	25
Calcium stearate, $C_{36}H_{70}O_4$	2

Calcium stearate, a type of soap and lubricant, was used as a burning rate modifier that also helped lubricate mixing of the composition, increasing particle packing and density. This has the effect of obstructing hot gasses from moving through the unreacted material, which would normally speed the burn rate (undesired in smoke production, since increased burn rates can lead to "flame-ups" instead of smoke production). Potassium chloride was added as a diluent, meaning is generally pyrotechnically inert and was also reported to reduce incandescence of the composition (recalling boron carbide as a potential "green" green-light emitter); since obstruction of sight and not illumination is the ultimate goal, this is a beneficial effect. However, KCl was also found to produce solid products (slag), detrimental to smoke production, so an appropriate balance between reducing incandescence and not generating too much solid products had to be evaluated.

SUMMARY: THE CHALLENGE AND OPPORTUNITY OF SMOKES

Smoke production presents quite a challenge to pyrotechnicians: using just the right chemicals to create just the right conditions, at just the right temperatures, to generate just the right products for creating the desired smoke. Not only do chemical considerations for heat production and products have to be taken into account, but in many cases, the toxicity of the starting materials or products is also a major factor: Smokes are *meant* to be dispersed in air where human or animal ingestion is very possible. However, these challenges also provide ample opportunity for creative and innovative pyrotechnicians to explore much safer, but still viable, smoke composition systems useable for military, commercial, and entertainment purposes.

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12 Sound Production

Bursts of red and blue aerial shells reflect in the water, as fans of gold comets fire beneath to complete the scene

> The entire world appears to have a fascination with fireworks, and most countries have at least one special day each year where the sky explodes in bright colors and noise. Man has had a fascination – and been in awe – of fire as well as loud, bright bursts in the night sky going way, way back in time. What is the appeal of fireworks? Yes, they are entertaining, but there is surely something deeper in the human soul that relates to our attraction to these bright explosions.

NOISE PRODUCTION: REPORTS

The most common and basic audible effect produced by pyrotechnic devices is a loud explosive noise ("boom" or "bang" in common parlance). In the technical terminology for noise effects, the explosive sound effect itself is a "report." The device that produces a report in the fireworks industry is a "salute," while in the military it is deemed a "simulator." The most typical composition used to produce a report, whether in civilian or military applications, is an oxidizer–metal mixture that is termed a "flash powder" (discussed in similar detail in the "White-Light Production" in Chapter 10).

A report is produced by igniting an explosive mixture, usually under confinement in a heavy-walled cardboard tube. Confinement allows pressure to build inside the container up to the breaking/bursting point, which lets out the overpressure that human ears perceive as sound. Potassium chlorate and potassium perchlorate are the most commonly used oxidizers for report compositions, as noise production requires a hot-and-fast reaction to provide the quick "punch" needed for noise (barium nitrate is also viable in the right mixtures). Report mixtures will produce a flash of light and a loud "bang" upon ignition. Black powder under substantial confinement also produces a report, but it does not have the bright light emission of a flash powder.

The key factors that cause a material to be considered a "flash powder" for generating reports include the following:

1. When confined in a tube and ignited, even in small quantities, a loud audible effect and a bright flash of light are observed. Example: a common firecracker.
2. The pyrotechnic composition contains an active oxidizer and a significant percentage of metal fuel in fine particle size (usually <270 mesh). Small-to-moderate amounts of additional chemicals, such as sulfur as an accelerant, may be present.
3. Flame temperatures are high, typically 3,000°C or greater.
4. The composition itself can mass-explode in a manufacturing setting, with the quantity necessary for such an event depending on a number of factors, including the metal particle size, confinement, and oxidizer–fuel ratio.
5. Shipping cartons that contain devices with significant charges of flash powder per unit can mass explode in transportation of storage. Again, what is a "significant" amount of powder per unit will depend on a number of factors, but the amount per unit can be as low as one gram or so for a heavily confined, energetic powder.

Understanding these factors, we can propose the "Conkling Definition for a Flash Powder:" Flash powder means a type of explosive composition commonly used to produce a report in a completed fireworks device. Flash powder consists of at least one oxidizer (such as potassium perchlorate or barium nitrate) and 25% or more by weight (of the formulation) of a metal powder fuel (such as aluminum or magnalium) that is less than 53 microns in size (i.e., passes through a 270-mesh sieve). Other fuels such as sulfur may also be present (Conkling, Regarding a default classification system for fireworks. April 2006).

"Flash powders" are true explosives, and they will explode violently if a sufficient quantity of powder (perhaps 100 g or more) is present in bulk form, even if unconfined. As examined before, the pyrotechnician may ask: Do flash powders deflagrate or fully detonate? For most everyone's purposes, save for research scientists examining the physics of the detonation process, the best answer may be "who cares—it explodes!" Flash powders are sensitive and highly energetic and *great* care is needed when working with them.

Chlorate-based flash mixtures are considerably more hazardous than perchlorate compositions because of their substantially lower ignition temperatures. However, flash powders made with *either* oxidizer must be considered *very* dangerous. They have killed many people at fireworks manufacturing plants in the United States and abroad. Mixing should only be done using remote means, and the smallest feasible amount of composition should be prepared at one time. Bulk flash powder should *never* be stored anywhere near operating personnel.

The well-known Chinese firecracker has traditionally used a mixture of potassium chlorate, sulfur, and aluminum. The chlorate combined with sulfur makes this mixture doubly dangerous for the manufacturer. The ignition temperature of the potassium chlorate/sulfur system is less than 200°C. The presence of aluminum—an excellent fuel—guarantees that the pyrotechnic reaction will rapidly propagate once it begins. Safety data from China is unavailable, but one has to wonder how many accidents have occurred from the preparation of this firecracker composition. The preparation of potassium chlorate–sulfur compositions was banned in Great Britain in 1894 because of the numerous accidents associated with this mixture.

Why have Chinese factories used the potassium chlorate–aluminum/sulfur composition? One reason is regulatory in origin. Regulations of the United States Consumer Product Safety Commission (CPSC) limit the explosive content of a consumer-type firecracker to a maximum of 50 mg of chemical composition.[1] It is difficult to reliably produce a decent “bang” from a paper-wrapped firecracker with such a small amount of chemical composition. The chlorate-containing composition, with a fine aluminum or magnalium powder, can do it. The hope is that the 50 mg explosive effect will satisfy the public’s desire to make a noise on the 4th of July, without the need for an emergency room visit if the device is misused in some way. Numerous tests on shipping cartons containing retail packages of 50-mg firecrackers have demonstrated that these products, as packaged for transportation, do not pose a mass-explosion hazard in a fire situation.

The CPSC has proposed amendments to the regulations under CPSC Docket 2006-0034, “Amendments to Fireworks Regulations,” with several comment periods and extensions granted due to the nature and interest of the regulations by fireworks manufacturers and users. The final rule has not been accepted as of the time of this writing, but the proposed rule and public comments are all available online (Regulations.gov 2017).

The standard American flash powder composition for “aerial salutes”—those intended to ignite in the air and not on the ground—is a blend of potassium perchlorate, sulfur or antimony sulfide, and aluminum. The ignition temperature of the formulation is several 100°C higher than chlorate-based mixtures, but these are still very dangerous compositions because of their extreme sensitivity to spark and flame. The spark sensitivity depends to a large extent on the particular metal powder that is used in the composition, with one study showing the spark sensitivity to be the greatest for very fine flake aluminum (Conkling and Jacobson, Investigation of the spark sensitivities of oxidizer/aluminum compositions April 2000). Ignition of a small portion of a flash powder mixture will rapidly propagate through the entire sample. These mixtures should only be prepared remotely, by experienced personnel.

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[1] Title 16, U.S. Code of Federal Regulations, Part 1500.17(a)(8).

TABLE 12.1
Flash and Sound Compositions

Composition		% by Weight	Use	Reference
I.	Potassium perchlorate, $KClO_4$	50	Military simulator	McIntyre (1980)
	Antimony sulfide, Sb_2S_3	33		
	Magnesium	17		
II.	Potassium perchlorate, $KClO_4$	64	M-80 firecracker for military training	McIntyre (1980)
	Aluminum	22.5		
	Sulfur	10		
	Antimony sulfide, Sb_2S_3	3.5		
III.	Potassium chlorate, $KClO_3$	43	Japanese “flash thunder” for aerial fireworks	Shimizu (1981)
	Sulfur	26		
	Aluminum	31		
IV.	Potassium perchlorate, $KClO_4$	50	Japanese “flash thunder” for aerial fireworks	Shimizu (1981)
	Sulfur	27		
	Aluminum	23		

By their nature, these mixtures are extremely dangerous to prepare, store, and transport and can be exceptionally sensitive to ignition by static electricity or other inputs. They should only be mixed by trained personnel using adequate protection.

Table 12.1 lists several “flash powder” formulas used to generate reports for different purposes. While the device specifications/engineering is not described, it is generally expected that these compositions would be confined in cardboard tubes to produce the required sound effect.

WHISTLES

A unique, whistling phenomenon (i.e., a high-pitched tone not unlike a human or train whistle) can be produced by firmly pressing certain oxidizer–fuel mixtures into open/vented cardboard tubes and igniting the compositions. When hot gas is quickly expelled from the container up the “chimney” and through the open vent, a synchronized vibration is achieved through gas turbulence, leading to the human ear hearing the characteristic “whistle.” A detailed analysis of this complex fluid-dynamics phenomenon, both from a chemical and physical view, has been published by Maxwell (Maxwell 1996), and a more recent review of the whistle literature has also been published (Davies 2005). Further whistle research has continued in efforts to fully understand the phenomenon (Domanico 1996) (Podlesak and Wilson 2004). Without consolidation of the powder in a tube, whistle composition produces a rapid flash of light (in an explosive manner) and no whistle-like effect. The whistle effect is produced by compositions consisting of potassium chlorate or potassium perchlorate as the oxidizer, with a salt of benzoic acid or a substituted benzoic acid as the fuel. Structures of two examples of these organic-salt fuels, potassium benzoate and sodium salicylate, are shown in Figure 12.1.

Whistle compositions were initially developed in the search for possible replacements for black powder in propellant applications. One can imagine the reaction of the first pyrotechnic chemist who blended what is now known to be whistle composition in a research setting, pressed the powder into a tube to examine its propellant characteristics, and then heard a loud, piercing screech when the composition was ignited!

Devices producing a whistle-like effect have since found uses both in the civilian arena for fireworks effects as well as in military applications for simulators used in training exercises to simulate incoming rounds. Titanium particles (in particle size greater than 100 mesh) can be added in low (5% of so) amount to whistle composition to produce a spark-fountain effect to accompany the audible output.

A reaction that produces a whistling effect is burning intermittently from layer to layer in the pressed composition. Because the gases have to be produced at a rapid rate to achieve the whistle phenomenon and the mixture is pressed into a semi-confined tube, a whistling composition is on the verge of an explosion. These mixtures *must* be cautiously prepared and carefully loaded into tubes. With the exception of flash powders, whistle compositions are perhaps the second-most energetic class of pyrotechnic compositions used by the commercial fireworks industry. Large quantities of bulk powder should be avoided, and they should never be stored near operating personnel. Several formulas for whistle compositions are given in Table 12.2.

CRACKLE EFFECTS

A relatively new effect in the field of entertainment pyrotechnics is a crackling effect (numerous snapping or popping sounds) produced by a “thermite”-type reaction

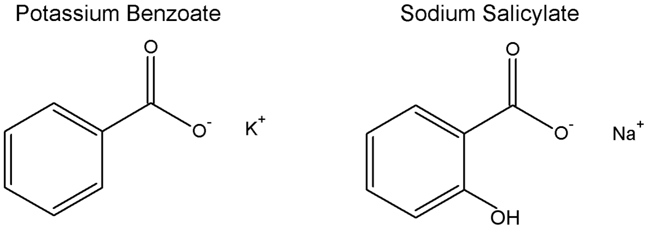

FIGURE 12.1 The molecular structures of potassium benzoate and sodium salicylate, both used as organic fuels in whistle compositions. These fuels will burn relatively quickly with appropriate oxidizers in a pressed form, though not so fast as to deflagrate nearly instantaneously. The quick burn and generation of hot gas helps produce the whistle effect from vibration and turbulence in the “fluid” gas mixture.

TABLE 12.2
Whistle Compositions

Composition		% by Weight	Note	Reference
I.	Potassium chlorate, $KClO_3$	73	Military simulator	McIntyre (1980)
	Gallic acid, $C_7H_6O_5 \cdot H_2O$	24		
	Red gum	3		
II.	Potassium perchlorate, $KClO_4$	70	Perhaps the safest to prepare and use	Shimizu (1981)
	Potassium benzoate, $KC_7H_5O_2$	30		
III.	Potassium perchlorate, $KClO_4$	75	Hygroscopic does not store well	Shimizu (1981)
	Sodium salicylate, $NaC_7H_5O_3$	25		
IV.	Potassium perchlorate, $KClO_4$	75	Chinese whistle composition	Self-reported
	Potassium hydrogen phthalate, $KC_8H_5O_4$	25		

These mixtures are very sensitive to ignition and can be quite dangerous to prepare. They should only be mixed by trained personnel using adequate protection.

between a metal oxide and a metal.[2] The original "crackle" compositions that were introduced into the fireworks market by China contained lead tetroxide—also known as "red lead" oxide—with formula Pb_3O_4 and magnalium as the fuel. Replacement formulations were later developed to remove the toxic lead, again based on thermite-type metal oxide–metal reactions, have been developed using bismuth(III) oxide and copper(II) oxide in place of lead tetroxide, again with magnalium as the fuel (Jennings-White 1992). The addition of coarse (>100 mesh) titanium metal particles with these compositions produce a spectacular white spark effect in addition to the crackling effect (T. Shimizu, Studies on mixtures of lead oxides with metals [magnalium, aluminum, or magnesium] 1990).

While an audible effect is produced when granules of crackling composition ignite, there is very little gas pressure produced from the thermite-type reaction, and consequently the small granules have little-to-no explosive effect on the surroundings. Bulk amounts of the crackling compositions in the manufacturing workplace, though, will burn very hot and very fast, and caution is definitely required when working with such mixtures. The reaction of bismuth oxide with a 50/50 alloy of magnalium is similar to:

$$2Bi_2O_3 + 3Mg + 2Al \rightarrow 2Bi + 3MgO + Al_2O_3 \qquad (12.1)$$

---

[2] "Dragon's Eggs" or "Pharaoh's Eggs" are based on this phenomenon.

TABLE 12.3
Crackle Compositions

Composition		% by Weight	Reference
I.	"Red Lead" Oxide—Pb_3O_4	82	Kosanke, et al. (2012)
	Magnalium, Mg/Al (>100 mesh)	9	
	Copper oxide, CuO	9	
II.	Bismuth oxide, Bi_2O_3	50	Self-reported
	Copper oxide, CuO	15	
	Magnalium, Mg/Al	20	
	Titanium (>100 mesh)	15	
	Binder/solvent	As needed	
III.	Bismuth subnitrate, $Bi_5O(OH)_9(NO_3)_4$	70	Jennings-White (1992)
	Magnalium, Mg/Al (60 mesh)	20	
	Copper oxide, CuO	10	

Crackle-effect compositions, both red-lead based and lead-free, are shown in Table 12.3. These compositions would be blended with solvent/binder, and the damp material would be tumbled or screened to form small granules, which are then dried for use.

While it is unclear exactly how the cracking effect is generated, two theories have been proposed. First, noting the thermite-type reaction in Equation 12.1, the bismuth oxide is reduced to elemental bismuth, but the reaction temperature (owing to the presence of magnalium) will be above the boiling point of bismuth, which is approximately 2,800°C. So, elemental bismuth is both quickly produced and immediately flash-boiled, rapidly expanding in air (before quickly cooling back to a solid), creating the pressure-burst sound effects that the human ear hears as a crackle. Second, large particles of metal, such as magnalium, titanium, or zirconium, appear to be a source of the crackling effect. Large granules of magnalium have been pinpointed as the source of the crackle in studies where the large granules have been observed breaking into smaller spark particles in air, incidentally generating the "crackle" (Kosanke, et al. 2012).

A FINAL NOTE ON STUDYING THE CHEMISTRY OF PYROTECHNICS

As the reader has hopefully seen by now, the study and application of pyrotechnic principles and energetic materials is a complex domain of chemical interactions and physical processes that can provide users with practical functions and observers with some fascinating effects. From relatively simple binary heat-and-light producing systems through complex smoke-and-sound compositions, the study of the chemistry of pyrotechnics has produced some remarkable advancement for the art and science of fire. However, as the “green pyrotechnics” developments have shown, there is still much work left to be done and many innovations to be found to make pyrotechnics an even better, safer, and more constructive discipline. We hope this text provides both a starting point as well as an ongoing reference for scientists, researchers, and enthusiasts to better understand and continually advance the chemistry of pyrotechnics.

13 Acknowledgments and Further Exploration

ACKNOWLEDGMENTS AND THANKS

This book is a continuation of the lifelong work and study of Dr. John Conkling. "Acknowledging" his work and thanking him for guidance barely scratches the surface of what Dr. Conkling has provided to me personally as a mentor and a friend, in service to Washington College, as both student and professor, in support of the community of Chestertown, MD, and in leadership to the international world of pyrotechnics over his decades-long career. Dr. Conkling is in every way a philosopher king.

Mrs. Sandy Conkling has also been a joy to work with, ever at Dr. Conkling's side assisting with the seminars, the American Pyrotechnics Association, and other day-to-day goings-on in the world of pyrotechnics. Mrs. Conkling was always inviting to me, helpful, and really quite a treasure!

Thank you to Joe "Dr. Pyro" Domanico for his instruction and friendship as a mentor during the Summer Pyrotechnic Seminar days. Joe has an unparalleled knack for finding the exuberance and joy in the world of pyrotechnics, never too busy to explain a little more detail or crack one more joke! The notes that I made in margins of books and scrap sheets of paper from Joe's missives while pyrotechnics combusted away behind him in a lab hood were *invaluable* to my own instruction and preparing this text. A picture of myself, Dr. Conkling, and Joe can be seen in Figure 13.1, following another successful Summer Pyrotechnic Seminar during the summer of 2011.

Thank you to Dr. Tyler Benedum, whose footsteps I followed at Washington College to work for Dr. Conkling, and then followed down to Charlottesville, and then out for the occasional NASCAR race. I'm not sure that I would have made the initial connection with Dr. Conkling without Tyler's friendship and mentorship.

Great appreciation goes to Dr. Jesse Sabatini for keeping me in the loop on the advancements of green pyrotechnics. Dr. Sabatini and his colleagues' work has truly advanced the state-of-the-art in pyrotechnics, and I expect the volume of his lifelong work to be held in the highest regard in pyrotechnics. Dr. Sabatini opened up my initial understanding of green pyrotechnics, which lead to many months of searching down the veritable rabbit hole of the wide world of environmentally friendly energetic materials.

Many thanks to the American Chemical Society (ACS) for taking an interest in the chemistry of pyrotechnics and sponsoring three different live webinars on pyrotechnics, which were all found to be enjoyable and useful by the audience. Thanks to my associates in the venture Erik Holderman, Tanya Fogg, Samuel Toba, Michael

FIGURE 13.1 Christopher J. Mocella, Dr. John Conkling, and Joe Domanico, following the 25th annual Summer Pyrotechnics Seminar held at Washington College, Chestertown, MD, in June 2011.

David, Darren Griffin, Andrew Maynard, and all the other support staff to this very fun venture.

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Thank you to my father for the good chemistry genes, and to my mother for the good English-grammar genes. Hopefully I have put them both to their proper use here!

Finally, I could not have done this without the support of my loving wife Kelly and son Joshua, who allowed me to steal away to my office to "work on the book" and always gave me that little extra encouragement. I love you both very much!

FURTHER RESOURCES FOR EXPLORING PYROTECHNICS

This book is intended to be a primer to the wide-reaching world of pyrotechnics, and specifically from the standpoint of chemistry. Numerous other texts, journals, groups, and public resources are available to the researcher to continue their study, a few of which are outlined below.

Two prominent authors featured in this text are Dr. Takeo Shimizu and A.A. Shidlovskiy, whose works are legend among pyrotechnics. Shidlovskiy's *Principles of Pyrotechnics*, translated from the original Russian, is an excellent primer into the theoretical principles as well as classic practical compositions for use. Dr. Shimizu published two seminal works, *Fireworks—The Art, Science, and Technique* and the four-part *Fireworks from a Physical Standpoint*. Both texts provide the scientific standpoint behind pyrotechnics as well as invaluable information on compositions and their physical properties.

Dr. Joseph McLain's *Pyrotechnics from the Viewpoint of Solid State Chemistry* additionally provides both academic and practical insight into pyrotechnics and energetic reactions. Dr. McLain was Dr. Conkling's mentor into the world of energetic materials at Washington College. Two other popular "classics" in the world of energetic materials are Tenney L. Davis' *The Chemistry of Powder & Explosives*, the combined work originally published in 1943, and Claude-Fortune Ruggieri's *Principles of Pyrotechnics*, originally published in 1821. These texts, while highly illuminating, will require a keen mental eye to both understand the chemistry as well as to handle the technical writing style of the times.

More recently, the *Journal of Pyrotechnics* has published several books in their Pyrotechnic Reference Series, including an *Illustrated Dictionary of Pyrotechnics* which was followed by a three-part *Encyclopedic Dictionary of Pyrotechnics*, and a *Pyrotechnic Chemistry* text further delving into fascinating technical detail on many of the concepts introduced here.

Several academic research journals are dedicated to pyrotechnics and energetic materials, constantly publishing new research and advancing the state-of-the-art. These include *Propellants, Explosives, Pyrotechnics* published by John Wiley & Sons, Inc., the *Journal of Pyrotechnics* published by Bonnie Kosanke (who, along with Ken Kosanke, are seminal researchers in the world of pyrotechnics), the *Journal of Energetic Materials* published by the Taylor & Francis Group, and the *International Journal of Energetic Materials and Chemical Propulsion* published by Begell House, Inc. Numerous other academic research journals will also periodically publish research in pyrotechnics in their scientific journals, such as those published by the American Chemical Society and the Royal Society of Chemistry.

A deep history of energetic materials (starting with black powder and including mainly explosives) can be found in G. I. Brown's *The Big Bang: A History of Explosives*. For a recent, post–Second World War history of the world of pyrotechnics and fireworks, one need look no further than Dr. John Conkling's *BOOM! America's Ever-Evolving Fireworks Industry.*

Numerous enthusiast and trade groups exist to support the pyrotechnics and fireworks communities. These groups are the core to the world of pyrotechnics, advancing the art, advocating for safety and environmental concerns, and providing a forum for discussion and presentation of their members' fascinating work (not to mention the fireworks shows). These include the Pyrotechnics Guild International (PGI), an international organization dedicated to the artistry, preservation, and enjoyment of fireworks. The PGI hosts annual conventions with truly spectacular fireworks displays (of course!). PGI manages numerous local clubs and affiliates and can be an excellent resource to begin working with pyrotechnics safely and properly through oversight by well-trained pyrotechnicians.

The American Pyrotechnics Association (APA) is an industry group whose mission is "to encourage safety in design & use of all types of fireworks, to provide industry information & support to its members, and to promote responsible regulation of the fireworks industry." The APA will advocate for fireworks companies through their work with the United States Congress and law enforcement agencies.

The International Pyrotechnics Society (IPS) is a research-focused organization (and whose official journal is *Propellants, Explosives, Pyrotechnics*) that intends to promote exchange of information, create resources for members use, encourage research in pyrotechnics, as well as hold the annual International Pyrotechnics Seminar that began in 1968. The published proceedings from these seminars are used throughout this text, highlighting the various scientific concepts and practical compositions involving pyrotechnics.

Numerous other local and international groups exist to promote pyrotechnics—British Pyrotechnics Society, Canadian Pyrotechnics Association, National Fireworks Association—all of which can be found by their presence on the internet.

Many collegiate and university academic research groups exist for the study of pyrotechnics, explosives, and energetic materials, both in the United States as well as around the world. These, along with military research outfits (such as divisions of the U.S. Army's Research, Development, and Engineering Command, RDECOM) are constantly researching and publishing their work in academic journals.

It would be impossible to list every resource and group involved in pyrotechnics, but this brief overview will hopefully point the reader in the right direction to begin their own journey into learning more about energetic materials and pyrotechnics. Please enjoy, have fun, be safe, and, as always:

Keep your powder dry.

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